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(PCT Rule 61.2)

To:

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International application No. PCT/ES99/00060	**Applicant's or agent's file reference**
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Applicant BAGAN VARGAS, Vicente et al	

1. The designated Office is hereby notified of its election made:

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Con informe de búsqueda internacional.

(54) Title: SILICA AND IRON OXIDE BASED PIGMENTS AND METHOD FOR THE PRODUCTION THEREOF

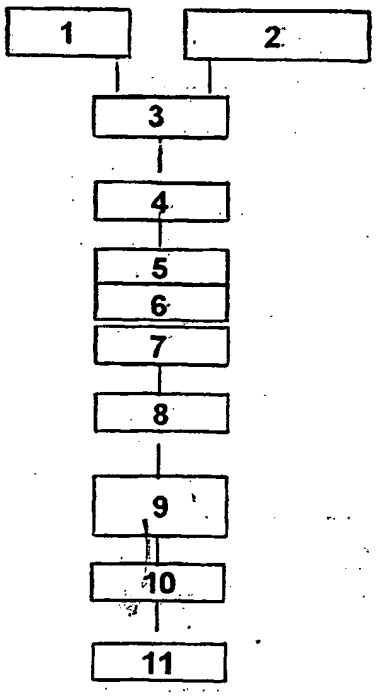
(54) Título: PIGMENTOS A BASE DE SILICE Y OXIDO DE HIERRO Y PROCEDIMIENTO DE FABRICACION DE LOS MISMOS

(57) Abstract

The invention relates to silica and iron oxide based pigments and to a method for the production thereof. In order to obtain a silica and iron oxide based pigment, microsilica and an iron oxide source are mixed and/or triturated in a ratio ranging between 2 % and 30 % by weight of iron oxide. A dry agglomerate is obtained by mixing the raw materials, which is calcined at temperatures ranging from 800° to 1300° C, yielding a product which is then triturated to obtain a reddish powder. This colorant has a wide variety of applications, for instance, red and orange colored pieces can be produced when it is added to a standard porcelain earthenware composition.

(57) Resumen

Para la obtención de un pigmento de sílice – óxido de hierro, se mezcla y/o moltura microsílice y una fuente de óxido de hierro en proporciones entre el 2 y el 30 % en peso de óxido de hierro. Con la mezcla de materias primas se obtiene un aglomerado seco que se calcina a temperaturas entre los 800 y los 1300 °C, obteniéndose un producto que se moltura para la obtención de un polvo de color rojizo. Este colorante puede utilizarse en una amplia variedad de usos, por ejemplo añadido a una composición standard de gres porcelánico, permite obtener piezas de coloraciones rojas y anaranjadas.



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PIGMENTOS A BASE DE SILICE Y OXIDO DE HIERRO Y PROCEDIMIENTO DE FABRICACION DE LOS MISMOS

Ambito de la invención

La presente invención se adscribe al sector técnico de la fabricación de pigmentos. En concreto se trata de obtener pigmentos de sílice y óxido de hierro útiles en diversas industrias y particularmente en la industria cerámica. El componente síliceo de estos pigmentos se obtendría a partir de microsílice o de humo de sílice, como rasgo más característicos de la invención.

Descripción del estado de la técnica

Los pigmentos naturales, sílice - hierro, son conocidos desde la antigüedad por sus propiedades cromóforas. Utilizados extensamente en cerámica, para la coloración de la masa, proporcionan un color en la gama de los ocres - marrones - naranjas - rojizos, al ser introducidos en proporciones considerables, que van del 2 al 12 % en peso, adolecen esencialmente de falta de homogeneidad debido a las oscilaciones en características físico-química de los yacimientos.

Numerosos esfuerzos han sido realizados, intentando reproducir las características de este tipo de colorantes naturales, aunque la limitación con la que se ha encontrado reiteradamente es la de conseguir productos de buena calidad a un coste competitivo en relación con los precios del mercado establecidos para los productos de origen natural.

En desarrollos previos existen distintos intentos de reproducción de este tipo de colorantes, basados en procedimientos de reacción por vía húmeda, con obtención de un gel, Fe_2O_3 $xSiO_2$, con contenido en Fe_2O_3 del 5 al 15% en peso, que debe someterse a un proceso de secado, calcinación

y molienda, para la obtención del producto de calidad adecuada.

En la patente US 3,005,724 (1961), se parte de sílice coloidal, como fuente de sílice, y de una fuente de óxido de hierro, preferentemente sulfato de hierro, obteniéndose una suspensión que se gelifica con la adición de una solución alcalina. Este gel se seca y calcina a temperaturas entre 900 y 1400°C y después se moltura para la obtención del pigmento.

Por otra parte, existen patentes en las que se utiliza la sílice pirogénica para mejorar las características de los pigmentos sintéticos de óxido de hierro. En estos casos, se utilizan bajas proporciones de sílice entre el 0,25 y el 10 % de SiO_2 en peso, y se utiliza para mejorar la fluidez y la coloración de los pigmentos, en comparación con los óxidos de hierro sintéticos.

En las patentes US 4.221.607 y US 4.229.635, se presentan procedimientos de obtención de éste tipo de óxido de hierro, partiendo de una solución de sulfato de hierro (caparrosa), como fuente de óxido de hierro, a la que se la adiciona una pequeña proporción de sílice (entre el 0,25 y el 10% en peso), para después de un proceso de secado y calcinación obtener los pigmentos de óxido de hierro, de propiedades mejoradas. En la patente US 4.221.607, la adición de sílice se realiza previamente al secado y calcinación y se obtiene un pigmento de hierro que se comporta mejor en el proceso de calcinación, mientras que en la patente US 4.229.635, la adición de hierro se realiza después del proceso de calcinación y durante un proceso de lavado del colorante, previo a un secado y molienda finales, obteniéndose un pigmento con fluidez mejorada.

No se han encontrado referencias en cuanto a la utilización de la microsílice para la fabricación de pigmentos de sílice - óxido de hierro.

Breve descripción de la invención

El objetivo de la presente invención ha sido la obtención de pigmentos inorgánicos del sistema sílice - óxido de hierro, X Fe_2O_3 Y SiO_2, utilizando como fuente de sílice, microsílice o humo de sílice, unido al proceso para la obtención industrial del mismo. Los pigmentos obtenidos desarrollan una coloración, rojo - anaranjada, sobre todo cuando se utilizan en la fabricación de productos cerámicos de baja porosidad, tipo gres porcelánico, siendo una alternativa competitiva, en calidad y coste, a los materiales naturales, tipo Gres de Thiviers que vienen empleándose actualmente. La presentación del producto se efectúa en forma de polvo micronizado, siendo susceptibles de poderse incorporar a la composición base por un mecanismo de dispersión directa, sin necesidad de molturación.

Descripción detallada de la invención

Los colorantes objeto de la invención, están constituidos principalmente por mezclas de oxido de silicio (sílice), en proporciones que oscilan entre el 70 y el 98% en peso, y óxido de hierro, en distintas proporciones, referido a una mezcla de SiO_2 y Fe_2O_3.

Esta invención utiliza como fuente de óxido de silicio la microsílice ó humo de sílice, que se obtiene, fundamentalmente como subproducto, por condensación de los gases desprendidos en el proceso de fabricación de silicio metal (fusión con arco eléctrico), y de aleaciones del silicio y otros metales. Dicho producto se caracteriza por su alto contenido en sílice (mayor del 90% expresado como SiO_2) y por su extraordinariamente fino tamaño de partícula (alrededor de 100 nm).

Como fuente de óxido de hierro se pueden utilizar óxidos de hierro rojos y/o amarillos (naturales y/o sintéticos) ó bien sales y/o complejos de hierro que pueden oxi-

darse y/o descomponerse durante el proceso de calcinación proporcionando el óxido de hierro.

A estas mezclas básicas se les pueden añadir pequeñas cantidades de aditivos, para mejorar las características del colorante y/o modificar su coloración.

Los colorantes resultantes, son pigmentos de coloración rojo - anaranjada, que se pueden utilizar para colorear todo tipo de materiales, preferentemente materiales cerámicos, y sobre todo masas cerámicas que proporcionen materiales cerámicos de baja porosidad, tipo Gres Porcelánico.

En función de la composición, fuente de óxido de hierro, condiciones de cocción y tratamiento posterior del colorante, se obtiene una amplia gama de coloraciones, dentro de los tonos rojo - anaranjados.

En esencia, la sílice proporciona un recubrimiento, capa protectora, a las partículas de óxido de hierro, que las protege frente a agresiones externas, como la temperatura, atmósfera y/o ataque de otros compuestos. Esta capa de protección, es la responsable de que el óxido de hierro procesado de este modo, permanezca más estable durante su uso en las composiciones cerámicas que son sometidas a altas temperaturas durante su proceso de elaboración.

Estos colorantes de sílice - hierro se obtienen por calcinación, de las mezclas de materias primas, a altas temperaturas, formándose un pigmento con estructura de tridimita y/o cristobalita, en la que el óxido de hierro está incorporado con estructura de hematita. La tridimita ó cristobalita se forman por calcinación de la sílice amorfa, obteniéndose una estructura estable u otra, en función de las condiciones de cocción y de los aditivos e impurezas presentes.

Las distintas composiciones de materia prima se pueden preparar mediante procesos vía seca o vía húmeda. En el proceso vía seca, se realiza la mezcla de materias primas en un molino o en una mezcladora, pudiéndose, opcionalmente, granular la mezcla resultante, para facilitar su

manipulación (transporte, dosificación,...). En el proceso vía húmeda, se prepara una suspensión en agua de las materias primas por molienda o dispersión, secándose la mezcla, en un proceso de atomización, en que se obtiene un material aglomerado, apto para su posterior procesado.

Estas mezclas de materias primas, más o menos aglomerada, pueden pasar opcionalmente a una etapa previa de secado, para proceder a continuación a su calcinación (tratamiento térmico a elevada temperatura, en el que van a producirse las distintas transformaciones físico-químicas que conducirán el material hasta su estado final). Dicha calcinación se puede efectuar en distintos tipos de hornos a temperaturas comprendidas entre los 800 y 1300°C, en función de las características de la sílice, de la fuente de óxido de hierro y de los aditivos utilizados.

En algunos casos se puede realizar una calcinación previa, a menor temperatura, para preparar adecuadamente las materias primas para su posterior reacción, procediéndose en esta etapa a oxidar la materia orgánica y el óxido de hierro presentes y/o a descomponer, en el caso que sea necesario, la materia prima fuente del óxido de hierro.

El producto después de la calcinación, se somete a una etapa de reducción del tamaño de partícula para proporcionar una coloración más homogénea. Dicha operación se efectúa, preferentemente, en una instalación de molienda de vía seca, con clasificación dinámica, que permite garantizar que más del 99% de las partículas estén por debajo de los 40 micrómetros.

Ejemplos

Ejemplo 1

87 kg. de microsílice ,13 kg. de óxido de hierro rojo sintético, se molturan en un molino de bolas de sílex durante 4 horas, con 50 litros de agua. La suspensión obtenida se seca y el granulado obtenido se calcina 1050°C con

un tiempo de permanencia a la temperatura máxima de 3 horas. Se obtiene un producto de coloración rojiza, que se moltura en un molino de bolas de alúmina vía seca, hasta que el 99% de las partículas esté por debajo de 40 micras. Este colorante adicionado a una composición Standard de gres porcelánico en proporción del 5% en peso, proporciona piezas cocidas con coordenadas cromáticas Hunter-LAB L=38,0 a=15,6 b=7,4.

Ejemplo 2

346 kg. de microsílice y 72 kg. de óxido de hierro rojo sintético, se granulan en una equipo de granulación intensivo con 80 litros de agua. El granulado obtenido se seca y calcina a 1025°C con un tiempo a la temperatura máxima de 6 horas. Se obtiene un producto de coloración rojiza, que se moltura de igual forma al ejemplo 1. Las coordenadas cromáticas que se obtienen son L=40.3 a=15.0 b=7.3.

Ejemplo 3

94 kg. de microsílice y 6 kg. de óxido de hierro rojo sintético se procesan de igual forma que en el ejemplo 1. Las coordenadas cromáticas que se obtienen son L=43.5 a=17.2 b=8.5.

Ejemplo 4

Se prepara una suspensión con 65.8 kg. de microsílice, 34.2 kg. de sulfato ferroso ($FeSO_4.7H_2O$) y 75.0 kg. de agua en un molino de bolas de silex, con un tiempo de molienda de 4 horas. La suspensión se seca y se obtiene un granulado que se precalcina para descomponer los sulfatos y oxidar el óxido de hierro y posteriormente se calcina a 1100°C. Las coordenadas cromáticas que se obtienen en las piezas cocidas preparadas con un 5% en peso de colorante son L=43.0 a=16.6 b=10.5.

Descripción de las figuras

Figura 1. Diagrama de bloques del proceso de fabricación utilizado.

1. Microsílice
2. Fuente de óxido de hierro
3. Molienda
4. Aglomeración
5. Precalcinación
6. Calcinación
7. Enfriamiento
8. Mezclado
9. Molienda Vía seca
10. Mezclado
11. Ensacado

REIVINDICACIONES

1. Pigmentos de sílice-óxido de hierro caracterizados por que el componente silíceo (SiO_2) se obtiene a partir de microsílice o humo de sílice, teniendo una proporción de óxido de silicio que oscila entre el 70 y el 98 % en peso, mientras que la proporción de óxido de hierro oscila entre el 2 y el 30 % en peso.

2. Procedimiento de obtención de los pigmentos de la reivindicación 1, caracterizado por comprender las siguientes etapas:

a) Mezclado de las materias primas mayoritarias y minoritarias
b) Aglomeración de la mezcla de materias primas resultante de la etapa anterior
c) Calcinación en horno de la mezcla aglomerada previamente en ciclo térmico a temperaturas comprendidas entre 800 y 1300°C, con tiempos de residencia oscilando entre 1 y 24 h.
d) Mezcla del pigmento obtenido en la etapa de calcinación anterior
e) Reducción del tamaño de partícula de la mezcla del pigmento obtenido
f) Mezcla final con control de las coordenadas cromáticas del pigmento obtenido
g) Dosificación y envasado

3. Procedimiento según la reivindicación 2, en el que las etapas a) y/o b) pueden hacerse por vía seca.

4. Procedimiento según la reivindicación 2, en el que las etapas a) y/o b) pueden hacerse por vía húmeda.

5. Procedimiento según las reivindicaciones 2 y 3, en el que la mezcla de la etapa a) se hace mediante molturación.

6. Procedimiento según las reivindicaciones 2 y 4, en el que la mezcla de la etapa a) se hace mediante dispersión, preferentemente en agua.

7. Procedimiento según las reivindicaciones 2, 3 y 5, en el que la aglomeración de la etapa b) consiste en una granulación.

8. Procedimiento según las reivindicaciones 2, 4 y 6, en el que la aglomeración de la etapa b) consiste en un secado por atomización.

9. Procedimiento según las reivindicaciones 2 a 8, en el que, opcionalmente, antes de la etapa c) se dispone una etapa previa de precalcinación.

10. Procedimiento según las reivindicaciones 2 a 9, en el que, opcionalmente, tras la etapa c) se dispone una etapa de enfriamiento, previa a la mezcla del pigmento resultante.

11. Procedimiento según las reivindicaciones 2 a 10, en el que la etapa e) consiste preferentemente en una molturación o molienda.

12. Pigmentos obtenidos según el procedimiento de las reivindicaciones 2 a 11.

13. Utilización de la microsílice como fuente de SiO_2 en la fabricación de pigmentos y/o colorantes inorgánicos.

14. Utilización del humo de sílice como fuente de SiO_2 en la fabricación de pigmentos y/o colorantes inorgánicos.

15. Utilización según las reivindicaciones 13 y 14, caracterizada porque la fuente de sílice se obtiene a partir de la condensación de los gases desprendidos en la fabricación de silicio metal y/o de aleaciones del mismo.

16. Utilización de los pigmentos de las reivindicaciones 1 o 12, solos o mezclados con otros materiales, como integrantes en las composiciones de esmaltes, vidrios, cerámicas, cementos, plásticos, laminados, tintas gráficas y caucho.

17. Utilización de los pigmentos de las reivindicaciones 1 o 12, solos o mezclados con otros materiales, en la decoración superficial de esmaltes, vidrios, cerámicas, cementos, plásticos, laminados, tintas gráficas y caucho.

18. Producto cerámico caracterizado por incluir en su composición los pigmentos de las reivindicaciones 1 o 12.

19. Producto cerámico de acuerdo con la reivindicación 18, caracterizado por consistir en un gres porcelánico.

20. Gres porcelánico de acuerdo con la reivindicación 19, caracterizado por presentar, para un porcentaje de pigmento del 2% que resulta en un color de tonos rojo-anaranjados, unas coordenadas cromáticas (Hunter-LAB) en los siguientes intervalos: L = 36-46, a = 10-18 y b = 7-11.

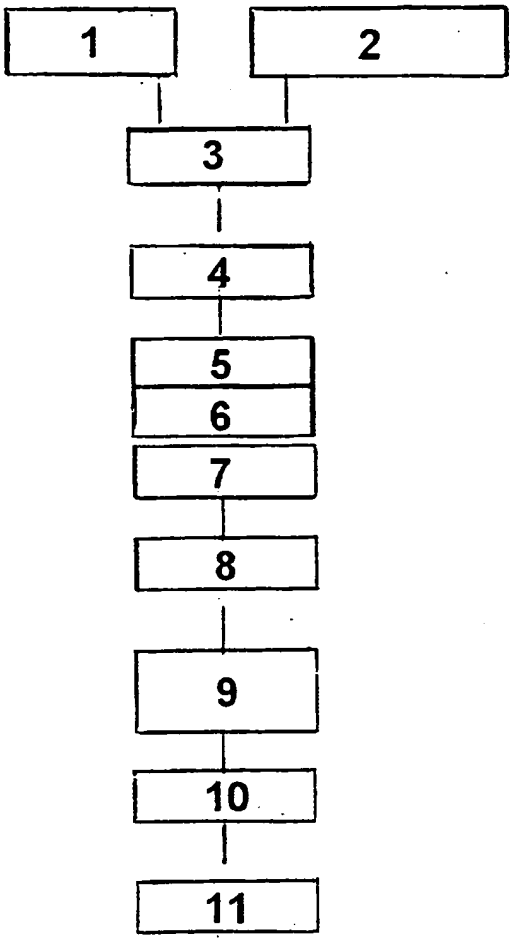

FIG. 1

INTERNATIONAL SEARCH REPORT

Inter... application No. U013610-2
PCT/ES 99/00060

A. CLASSIFICATION OF SUBJECT MATTER [6]:
IPC 6 : C09C 1/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC6 :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BONDIOLI, F. et al, shyntheses of Fe_2O_3/ Silica red inorganic inclusion pigments for ceramic applications, Mater. Res. Bull. (1998), 33(5), 723-729; see the whole document	1,14
Y		2-12,16,17
X	US 4221607 A (DICKERSON) 09 September 1980 (09.09.80) , Column 2, line 48 - column 5, line 25	14
Y		2-12,16,17
X	US 5342597 A (TUNISON, III) 30 August 1994 (30.08.94); column 2, lines 3-21	14
A	US 4405729 A (SCHWEITZER) 20 September 1983 (20.09.83); column 2, line 40 - column 3, line 58	1,12,14,17
A	US 4119712 A (GOLDNER et al.) 10 October 1978 (10.10.78); claims 3	1,14

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
25 October 1999 (25.10.99)	24 November 1999 (24.11.99)
Name and mailing address of the ISA/ S.P.T.O.	Authorized officer

Patent document cited in search report	Publication date	Patent familiy member(s)	Publication date
US 4221607 A	09.09.1980	NONE	
US 5342597 A	30.08.1994	NONE	
US 4405729 A	20.09.1983	NONE	
US 4119712 A	10.10.1978	AR 215732 A	31.10.1979
		AU 39046/78 A	21.02.1980
		AU 522794 B	24.06.1982
		BR 7805554 A	11.03.1980
		CA 1111770 A	03.11.1981
		DE 2836497 A	06.03.1980
		FR 2433337 A,B	14.03.1980
		GB 2027341 A,B	20.02.1980
		IT 1098385 A	07.09.1985
		JP 55035001 A	11.03.1980
		JP 62018525 B	23.04.1987
		ZA 7804537 A	29.08.1979

INFORME DE BÚSQUEDA INTERNACIONAL

Solicitud internacional nº
PCT/ ES 99/00060

A. CLASIFICACIÓN DEL OBJETO DE LA SOLICITUD

CIP[6] C09C 1/62
De acuerdo con la Clasificación Internacional de Patentes (CIP) o según la clasificación nacional y la CIP.

B. SECTORES COMPRENDIDOS POR LA BÚSQUEDA

Documentación mínima consultada (sistema de clasificación, seguido de los símbolos de clasificación)

CIP[6]

Otra documentación consultada, además de la documentación mínima, en la medida en que tales documentos formen parte de los sectores comprendidos por la búsqueda

Bases de datos electrónicas consultadas durante la búsqueda internacional (nombre de la base de datos y, si es posible, términos de búsqueda utilizados)

CIBEPAT, EPODOC, WPI, PAJ, CAPLUS

C. DOCUMENTOS CONSIDERADOS RELEVANTES

Categoría*	Documentos citados, con indicación, si procede, de las partes relevantes	Relevante para las reivindicaciones nº
X	BONDIOLI, F. et al, Shyntheses of Fe_2O_3 / Silica red inorganic inclusion pigments for ceramic applications, Mater. Res. Bull. (1998), 33(5), 723-729; todo el documento	1,14
Y		2-12,16,17
X	US 4221607 A (DICKERSON) 09.09.1980, columna 2, línea 48 - columna 5, línea 25	14
Y		2-12,16,17
X	US 5342597 A (TUNISON, III) 30.08.1994; columna 2, línea 3-21	14
A	US 4405729 A (SCHWEITZER) 20.09.1983; columna 2, línea 40 - columna 3, línea 58	1,12,14,17
A	US 4119712 A (GOLDNER et al.) 10.10.1978; reivindicación 3	1,14

☐ En la continuación del recuadro C se relacionan otros documentos ☒ Los documentos de familia de patentes se indican en el anexo

* Categorías especiales de documentos citados:

"A" documento que define el estado general de la técnica no considerado como particularmente relevante.

"E" solicitud de patente o patente anterior pero publicada en la fecha de presentación internacional o en fecha posterior.

"L" documento que puede plantear dudas sobre una reivindicación de prioridad o que se cita para determinar la fecha de publicación de otra cita o por una razón especial (como la indicada).

"O" documento que se refiere a una divulgación oral, a una utilización, a una exposición o a cualquier otro medio.

"P" documento publicado antes de la fecha de presentación internacional pero con posterioridad a la fecha de prioridad reivindicada.

"T" documento ulterior publicado con posterioridad a la fecha de presentación internacional o de prioridad que no pertenece al estado de la técnica pertinente pero que se cita por permitir la comprensión del principio o teoría que constituye la base de la invención.

"X" documento particularmente relevante; la invención reivindicada no puede considerarse nueva o que implique una actividad inventiva por referencia al documento aisladamente considerado.

"Y" documento particularmente relevante; la invención reivindicada no puede considerarse que implique una actividad inventiva cuando el documento se asocia a otro u otros documentos de la misma naturaleza, cuya combinación resulta evidente para un experto en la materia.

"&" documento que forma parte de la misma familia de patentes.

Fecha en que se ha concluido efectivamente la búsqueda internacional. 25 Octubre 1999 (25.10.1999)	Fecha de expedición del informe de búsqueda internacional 24 NOV 1999 24. 11. 99
Nombre y dirección postal de la Administración encargada de la búsqueda internacional O.E.P.M. C/Panamá 1, 28071 Madrid, España. nº de fax +34 91 3495304	Funcionario autorizado N. VERA GUTIÉRREZ nº de teléfono + 34 91 3495475

Formulario PCT/ISA/210 (segunda hoja) (julio 1998)

Documento de patente citado en el informe de búsqueda	Fecha de publicación	Miembro(s) de la familia de patentes	Fecha de publicación
US 4221607 A	09.09.1980	NINGUNO	
US 5342597 A	30.08.1994	NINGUNO	
US 4405729 A	20.09.1983	NINGUNO	
US 4119712 A	10.10.1978	AR 215732 A	31.10.1979
		AU 39046/78 A	21.02.1980
		AU 522794 B	24.06.1982
		BR 7805554 A	11.03.1980
		CA 1111770 A	03.11.1981
		DE 2836497 A	06.03.1980
		FR 2433337 A,B	14.03.1980
		GB 2027341 A,B	20.02.1980
		IT 1098385 A	07.09.1985
		JP 55035001 A	11.03.1980
		JP 62018525 B	23.04.1987
		ZA 7804537 A	29.08.1979

PATENT COOPERATION TREATY

U013610-2

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:
DE ELZABURU, Alberto
Calle Miguel Angel, 21
E-28010 Madrid
ESPAGNE

ELZABURU
Entrada
22.09.00 078349
ACH

Date of mailing (day/month/year) 14 September 2000 (14.09.00)	
Applicant's or agent's file reference PCT-50	**IMPORTANT NOTICE**
International application No. PCT/ES99/00060	**International filing date** (day/month/year) 10 March 1999 (10.03.99)
Priority date (day/month/year)	
Applicant ITACA, INNOVACIONES TECNICAS APLICADAS A CERAMICAS AVANZADAS, S.A. et al	

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   AU,KP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CU,CZ,DE,DK,EA,EE,EP,ES,FI,GB,GE,GH,GM,HR,
   HU,ID,IL,IS,JP,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MD,MG,MK,MN,MW,MX,NO,NZ,OA,PL,PT,RO,
   RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,UA,UG,UZ,VN,YU,ZW
   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   14 September 2000 (14.09.00) under No. WO 00/53680

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
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Authorized officer
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U013610-2

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PCT-50		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/ES99/00060	10/03/2000	10/03/1999
International Patent Classification (IPC) or national classification and IPC C09C1/62		
Applicant ITACA, INNOVACIONES TECNICAS APLICADAS A ...		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
09/10/2000	27.06.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Krafka, B Telephone No. +49 89 2399 8140

EL728144258

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ES99/00060

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-7	with telefax of	15/06/2001

Claims, No.:

1-20	with telefax of	15/06/2001

Drawings, sheets:

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-13,15-20
	No:	Claims	14
Inventive step (IS)	Yes:	Claims	1-13,15-20
	No:	Claims	14
Industrial applicability (IA)	Yes:	Claims	1-20
	No:	Claims	

2. Citations and explanations
   see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive st p or industrial applicability; citations and explanations supporting such statem nt

1) Reference is made to the following documents:

D1: 'Synthesis of Fe_2O_3/Silica red inorganic inclusion pigments for ceramic application','BONDIOLI F. ET AL.',MATER. RES. BULL., 33/5/00-00-1998, 723-729.

D2: US-A-4221607

2) Novelty - Art. 33 (1) and (2) PCT

2.1. D1 discloses red inorganic ceramic pigments in which haematite is included in a fumed silica matrix. Starting materials in the disclosed process are fumed silica and synthetic goethite which are blended by wet-mixing prior to heating and subsequent cooling (abstract, p. 724 paragraph 3). The thermal inclusion occurs at calcination at 1150-1200°C for 2-4 h (abstract). The pigments are suitable for use as colouring agents in enamels and in decoration (p. 723 paragraph 1 and p. 726 paragraph 2-5). The iron oxide content is 10 wt.% (p. 725 paragraph 1). L-a-b chromaticity values are surveyed (p. 727 paragraph 2 and Fig. 4 and 5). However, D1 does not disclose the use of microsilica as the starting material as defined in the present application. Therefore, in the light of D1, the subject-matter of claims 1-13 and 15-20 is regarded as novel.

2.2. D2 discloses silica-iron oxide pigments for which fumed silica serves as a starting product, but the ratios of silica (0.25 - 10 wt.%) and of iron oxide in the product are not the same as in the present application. In the process of D2 fumed silica or precipitated silica is blended with an iron oxide solution. The blend is then dried and subsequently calcined in a furnace at 718- 871 °C with a residence time of e.g. 4 h (ex. 1). The calciner output is then wet- ground in water to a desired particle size range (c. 3 l. 11-c. 4 l. 4). Thus, D2 does also not disclose the features by which the present invention is defined. In particular, D2 does not disclose the use of microsilica as the starting material and it does not disclose the ratio of silica and iron oxide as defined in the present application. Therefore, also in the

light of D2, the subject-matter of claims 1-13 and 15-20 is regarded as novel.

2.3. Claim 14 relates to the use of fumed silica as a source of SiO_2 in the manufacture of inorganic pigments and/or colorants. Therefore, in the light of what was set forth under 2.1 and 2.2, the subject-matter of claim 14 cannot be regarded as novel.

3) Inventive Step - Art. 33 (1) and (3) PCT

3.1. The technical problem underlying the present invention can be seen in providing inorganic pigments of silica-iron oxide having a red-orange hue colouration. This problem is overcome by the present invention by the use of microsilica as the silica source and iron oxide for producing pigments having a ratio of silica of 70-98 wt.% and a ratio of iron oxide of 2-30 wt.%. Furthermore, a process for obtaining such a pigment and products derived from the pigments are defined.
Document D1 is considered to represent the closest prior art.

3.2. The disclosures of D1 and D2 have been set forth in detail above. However, it is stated in D1 (p. 727 last paragraph), that the stability of pigments is decreased in samples obtained by using silica having surface area lower than 300 m^2/g and heat treated at 1300°C (as is the case in the present invention). Microsilica, as is used in the present invention, typically has a surface area in the range of 0.015-10 m^2/g. Surprisingly, the pigments subject of the present invention show colour features and stabilities similar to the prior art products based on high surface fumed silica. Therefore, the subject-matter of claims 1-13 and 15-20 is regarded as involving an inventive step.

Re Item VIII
Certain observations on the international application

a. One of the features of claim 20 ("for a percentage pigment of 2% that gives a colour of red-orange tone") is not referred to in the description. Claim 20 is therefore not supported by the description as required by Article 6 PCT.

PIGMENTS BASED ON SILICA AND IRON OXIDE AND PROCESS FOR THE MANUFACTURE THEREOF

Field of the Invention

The present invention relates to the technical field of pigment manufacturing. Specifically, it deals with obtaining silica and iron oxide pigments useful in different industries and particularly in the ceramics industry. The silica component of these pigments would be obtained from microsilica or from fumed silica as the most characteristic feature of the invention.

Description of the state of the art

The natural pigments, silica B iron, have been known since ancient times for their chromophore properties. Extensively used in ceramics for colouring the mass, they provide a colour within the range of ochre B browns B oranges B reddish, on being introduced in high ratios which range from 2 to 12% by weight. However, they essentially lack homogeneity due to variations in the physico-chemical characteristics of the deposits.

Several efforts have been carried out trying to reproduce the features of this type of natural colorants, although these efforts have always come up against the limitation of achieving good quality products at a competitive cost relative to the market prices established for naturally occuring products.

In the prior developments there are different attempts to reproduce this type of colorants based on wet reaction processes, obtaining a gel, Fe_2O_3, $xSiO_2$, with a Fe_2O_3 content of 5 to 15% by weight, which must be submitted to a drying, calcination and milling process in order to obtain the product with an adequate quality.

In US patent 3,005,724 (1961), the starting product is a colloidal silica as a silica source, and a source of iron oxide, preferably iron sulphate, obtaining a suspension

which is gelified by the addition of an alkaline solution. This gel is dried and calcinated at temperatures between 900 and 14001 C and afterwards it is milled in order to obtain the pigment.

On the other hand, there are patents in which fumed silica is used to improve the features of the iron oxide synthetic pigments. In these cases, low silica ratios between 0.25 and 10 % of SiO_2 by weight are used, and it is used to improve the flowability and the coloration of the pigments in comparison with the synthetic iron oxides.

US patents 4,221,607 and 4,229,635, are disclosing processes for obtaining this type of iron oxide, starting from a solution of copperas as a source of iron oxide, to which a small proportion of silica is added (between 0.25 and 10% by weight) to obtain the iron oxide pigments with improved properties after a drying and calcination process. In US patent 4,221,607, the addition of silica is carried out before drying and calcination and an iron pigment is obtained which behaves better in the calcination process, while in US patent 4,229,635, the addition of iron is carried out after the calcination process and during a washing process of the colorant, before final drying and milling, obtaining a pigment with improved flowability.

References have not been found to the use of microsilica for the manufacture of silica-iron oxide pigments.

Brief description of the invention

The object of the present invention was to obtain inorganic pigments of the silica-iron oxide, Fe_2O_3 and SiO_2 system, using microsilica or fumed silica as the silica source, along with the process for industrial obtention of said pigment. The obtained pigments may have a of red B orange hue colouration, above all when used in the manufacture of ceramic products of low porosity such as porcelain stoneware. They are a competitive alternative, in

terms of quality and cost, to natural materials such as Thiviers stoneware, which are currently used. The presentation of the product is in the form of a micronised powder. The product can be incorporated into the base composition through a direct dispersion mechanism without the need for milling.

Detailed description of the invention

The colorants object of the invention consist mainly of mixtures of silicon oxide (silica), in ratios that range between 70 and 98 % by weight, and iron oxide, in different ratios, referred to a mixture of SiO_2 and Fe_2O_3.

This invention uses microsilica or fumed silica as the silicon oxide source. Which is basically obtained as a by-product by condensation of the gases evolved during the process of manufacturing silicon metal (electric arc melting) and alloys of silicon and other metals. Said product is characterised by its high content in silica (greater than 90 % expressed as SiO_2) and by its extremely fine particle size (around 100 nm).

As a source of iron oxide, red and/or yellow iron oxide (natural and/or synthetic) at ranges between 2 and 30% by weight can be used, or salts and/or complexes of iron that can be oxidised and/or decompose during the calcination process to provide iron oxide.

Small quantities of additive can be added to these basic mixtures to improve the features of the colorant and/or to modify its coloration.

The resulting colorants are pigments of a red-orange colour which can be used for colouring all sorts of materials, preferably ceramic materials, and specially ceramic masses that provide porcelain stoneware type low porosity ceramic materials. Particularly porcelain stoneware which show chromatic coordinates (Hunter-LAB) in the following ranges: L = 36-46, a = 10-18 and b = 7-11 are

obtained using those pigments of the invention. The pigments of the invention may be used, alone or in blends with other materials as integrant in the compositions or for the surface decoration of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

Depending on the composition, source of iron oxide, conditions of subsequent firing and treatment to which the colorant is submitted, a wide range of colours can be obtained within the red-orange tones.

In essence, the silica provides a protective coating layer for the iron oxide particles, protecting against external aggressions such as temperature, atmosphere and/or attack by other compounds. This protective layer ensures that the iron oxide processed in this way, remains more stable during its use in ceramic compositions that are submitted to high temperatures during their manufacture.

These colorants of silica-iron are obtained by calcination of mixtures of raw materials at high temperatures, forming a pigment with tridymite and/or crystobalite structure in which the iron oxide is incorporated with hematite structure. The tridymite or crystobalite are formed by calcination of the amorphous silica, obtaining a stable structure or another one, depending on the firing conditions and on the present additives and impurities.

The different compositions of raw material can be prepared through dry or wet processes. In the dry process, the mixture of raw materials is carried out in a mill or a blender. The resulting mixture may optionally be granulated to facilitate its handling (transport, dosing...). In the wet process, a suspension in water of the raw materials is prepared by milling and dispersion, drying the mixture in an atomisation process, in which an agglomerated material suitable for subsequent processing is obtained.

These mixtures of raw materials, more or less agglomerated, may optionally pass through a prior drying stage, to then proceed to calcination (thermal treatment at high temperature in which the different physico-chemical transformations that convert the material into its finished state will take place). Said calcination may be carried out in different oven types at temperatures comprised between 800 and 13001 C, depending on the features of the silica, the source of iron oxide and the used additives, with residence times ranging between 1 and 24h.

In some cases, a prior calcination may be effected, at a lower temperature to suitably prepare the raw materials for their subsequent reaction. In this stage, if necessary, the present organic material and the iron oxide are oxidised and/or the raw material acting as a source of iron oxide is decomposed.

After calcination the product is submitted to a particle size reduction step to provide a more homogeneous colour. Said operation is preferably carried out in a dry milling installation, with dynamic classification which permits to assure that more than 99 % of the particles are smaller than 40 micrometers. The process concludes with final blending with control of the chromaticity coordinates of the obtained pigment and dosing and packaging.

Examples

Example 1

87 kg of microsilica and 13 kg of synthetic red iron oxide are milled in a silex-ball mill for 4 hours with 50 litres of water. The suspension obtained is dried and the granulate obtained calcinated at a maximum temperature of 10501 C for three hours. A red coloured product is obtained, which is milled in a mill with alumina balls in dry conditions, until 99 % of the particles are smaller than 40 microns. This colorant, added to a standard composition of porcelain stoneware in a ratio of 5 % by weight, provides

fired pieces with Hunter-LAB chromaticity coordinates of L=38.0 a=15.6 b=7.4.

Example 2

346 kg of microsilica and 72 kg of synthetic red iron oxide are granulated in an intensive granulation machine with 80 litres of water. The granulate obtained is dried and calcinated at 10251 C for 6 hours at this maximum temperature. A reddish coloured product is obtained, which is milled in the same way as example 1. The chromaticity coordinates that are obtained are L=40.3, a=15.0 and b=7.3.

Example 3

94 kg of microsilica and 6 kg of synthetic red iron oxide are processed in the same way as in example 1. The chromaticity coordinates that are obtained are L=43.5, a=17.2 and b=8.5.

Example 4

A suspension is prepared with 65.8 kg of microsilica, 34.2 kg of ferrous sulphate ($FeSO_4\$7H_2O$) and 75.0 kg of water in a silex-ball mill. The milling lasts 4 hours. The suspension is dried and a granulate obtained that is pre-calcinated to decompose the sulphates and to oxidise the iron oxide and then the mixture is calcinated at 11001 C. The chromaticity coordinates that are obtained for the fired pieces prepared with 5% by weight of colorant are L.43.0, a=16.6 and b=10.5.

Description of the figures

Figure 1. Block diagram of the manufacturing process used.

1. Microsilica
2. Source of iron oxide
3. Milling
4. Agglomeration
5. Pre-calcination
6. Calcination

7. Cooling
8. Blending
9. Dry milling
10. Blending
11. Sacking

CLAIMS

1. Pigments of silica-iron oxide characterised in that the silica component (SiO_2) is obtained from microsilica, having a ratio of silica that ranges between 70 and 98% by weight, while the ratio of iron oxide ranges between 2 and 30% by weight.

2. A process for obtaining pigments of claim 1, characterised in that it comprises the following steps:

a) Blending the majority and minority raw materials, containing microsilica and iron oxide

b) Agglomerating of the resulting blend of raw materials from the previous stage

c) Calcinating in an oven the agglomerated blend obtained in the previous stage with a thermal cycle at temperatures comprised between 800 and 1300°C, with residence times ranging between 1 and 24 h,

d) Blending the pigment obtained in the previous calcination step,

e) Reducing the particle size of the obtained blend of pigment,

f) Final blending with control of the chromaticity coordinates of the obtained pigment,

g) Dosing and packaging.

3. A process according to claim 2, in which stages a) and/or b) may be carried out in dry conditions.

4. A process according to claim 2, in which stages a) and/or b) may be carried out in wet conditions.

5. A process according to claims 2 and 3, in which the blend from stage a) is carried out by milling.

6. A process according to claims 2 and 4, in which the mixture from stage a) is carried out by dispersion, preferably in water.

7. A process according to claims 2, 3 and 5, in which the agglomeration of stage b) consists of a granulation.

8. A process according to claims 2, 4 and 6, in which the agglomeration of stage b) consists of drying by atomisation.

9. A process according to claims 2 to 8, in which, before stage c) there is a prior pre-calcination step.

10. A process according to claims 2 to 9, in which, after stage c), there is a cooling step, prior to blending of the resulting pigment.

11. A process according to claims 2 to 10, in which step e) preferably consists of grinding or milling.

12. Pigments obtained according to the process of claims 2 to 11.

13. Use of microsilica as a source of SiO_2 in the manufacture of inorganic pigments and/or colorants.

14. Use of fumed silica as a source of SiO_2 in the manufacture of inorganic pigments and/or colorants.

15. Use according to claims 13 and 14, characterised in that the source of silica is obtained from condensation of gases evolved during the manufacture of silicon metal and/or alloys thereof.

16. Use of the pigments of claims 1 or 12, alone or in blends with other materials, as integrants in the compositions of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

17. Use of the pigments of claims 1 or 12, alone or in blends with other materials, in the surface decoration of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

18. A ceramic product characterised in that it includes in its composition the pigments of claims 1 or 12.

19. A ceramic product in accordance with claim 18, characterised in that it consists of a porcelain stoneware.

20. A porcelain stoneware in accordance with claim 19, characterised in that it shows chromatic coordinates (Hunter-LAB) in the following ranges: L = 36-46, a = 10-18 and b = 7- 11, for a percentage pigment of 2% that gives a colour of red-orange tone.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

ELZABURU MARQUEZ, Alberto
Miguel Angel, 21
E - 28010 Madrid
ESPAGNE

ELZABURU Entrada 02.07.01 812920 A|CH

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	27.06.2001
Applicant's or agent's file reference: PCT-50	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/ES99/00060	10/03/2000	10/03/1999

Applicant
ITACA, INNOVACIONES TECNICAS APLICADAS A ...

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Koutsoftas, P Tel.+49 89 2399-7273

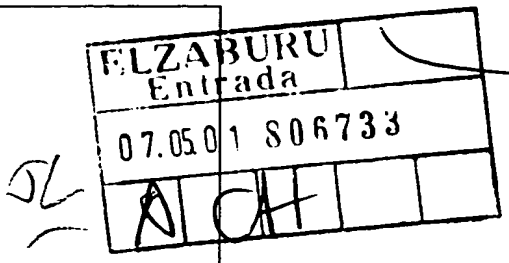
Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

ELZABURU MARQUEZ, Alberto
Miguel Angel, 21
E - 28010 Madrid
ESPAGNE



PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing *(day/month/year)*	02.05.2001
Applicant's or agent's file reference: PCT-50	**REPLY DUE** **within 1 month(s) and 15 days** from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/ES99/00060	10/03/2000	10/03/1999

International Patent Classification (IPC) or both national classification and IPC

C09C1/62

Applicant

ITACA, INNOVACIONES TECNICAS APLICADAS A ...

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

I	☒	Basis of the opinion
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain document cited
VII	☐	Certain defects in the international application
VIII	☒	Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 10/07/2001.

Name and mailing address of the international preliminary examining authority:
European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner
Krafka, B

Formalities officer (incl. extension of time limits)
Christensen, J
Telephone No. +49 89 2399 8052

I. Basis of the opinion

1. With regard to the **elements** of the international application (Replacement *sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*):

Description, pages:

1-6 as originally filed

Claims, No.:

1-20 as originally filed.

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1,14,16,17:NO; 2-13,15,18-20:YES
Inventive step (IS)	Claims	2-13,15,18-20:NO
Industrial applicability (IA)	Claims	1-20:YES

2. Citations and explanations
   see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive st p or industrial applicability; citations and explanations supporting such statem nt

1) Reference is made to the following documents:

D1: 'Synthesis of Fe_2O_3/Silica red inorganic inclusion pigments for ceramic application','BONDIOLI F. ET AL.',MATER. RES. BULL., 33/5/00-00-1998, 723-729.

D2: US-A-4221607

2) Novelty - Art. 33 (1) and (2) PCT

2.1. D1 discloses red inorganic ceramic pigments in which haematite is included in a fumed silica matrix. Starting materials in the disclosed process are fumed silica and synthetic goethite which are blended by wet-mixing prior to heating and subsequent cooling (abstract, p. 724 paragraph 3). The thermal inclusion occurs at calcination at 1150-1200°C for 2-4 h (abstract). The pigments are suitable for use as colouring agents in enamels and in decoration (p. 723 paragraph 1 and p. 726 paragraph 2-5). The iron oxide content is 10 wt.% (p. 725 paragraph 1). L-a-b chromaticity values are surveyed (p. 727 paragraph 2 and Fig. 4 and 5). Therefore, in the light of D1, the subject-matter of claims 1, 14, 16 and 17 is not novel.

3) Inventive Step - Art. 33 (1) and (3) PCT

3.1. The technical problem underlying the present invention can be seen in providing inorganic pigments of silica-iron oxide having a red-orange hue colouration. This problem is overcome by the present invention by the use of micro silica or fumed silica as the silica source and iron oxide for producing pigments having a ratio of silica of 70-98 wt.% and a ratio of iron oxide of 2-30 wt.%. Furthermore, a process for obtaining such a pigment and products derived from the pigments are defined. Document D1 is considered to represent the closest prior art.

3.2. The disclosure of D1 has been set forth in detail under 2.1. D2 discloses silica-iron oxide pigments for which fumed silica serves as a starting product, but the ratios

of silica (0.25 - 10 wt.%) and of iron oxide in the product are not the same as in the present application. However, a person skilled in the art would consider the process features disclosed in D2 as typical features for the production not only of the pigments of D2 but also for pigments with higher silica content and lower iron oxide content as is subject-matter of D1 and of the present application. In the process of D2 fumed silica or precipitated silica is blended with an iron oxide solution. The blend is then dried and subsequently calcined in a furnace at 718-871 °C with a residence time of e.g. 4 h (ex. 1). The calciner output is then wet-ground in water to a desired particle size range (c. 3 l. 11-c. 4 l. 4). Process parameter like agglomerating, final blending, dosing and packaging or drying by means of atomisation come within the scope of the customary practice followed by persons skilled in the art, especially as the advantages thus achieved can readily be foreseen. A surprising technical effect which is requisite for the presence of an inventive step, could not be seen. Therefore, over the combination of the technical teachings of D1 and D2, an inventive step cannot be acknowledged for the subject-matter of claims 2-11, and accordingly also not for the subject-matter of claim 12, which claims the product obtained by the process of claims 2 to 11.

3.3. As set forth above under 2.1, fumed silica serves in D1 as a source for SiO_2 in the manufacture of inorganic pigments. The use of micro silica as an alternative material for the same purpose does not seem to involve an inventive step. Furthermore, it does not seem to lead to any surprising technical effect when the fumed silica is obtained in a certain way. The subject-matter of claims 13 and 15 does therefore not fulfill the requirements of Article 33 (1) and (3) PCT.

3.4. Products such as ceramic products or porcelain stoneware are regarded as typical objects to which red coloured inorganic pigments are applied. The chromatic coordinates do not appear to represent surprising optical properties (see e.g. D1 Fig. 4 and 5) which could justify an inventive step. Therefore, an inventive step has to be denied for the subject-matter of claims 18, 19 and 20.

Re Item VIII

Certain observations on the international application

a. Certain features of claim 1 ("ratio of iron oxide ranges between 2 and 30% by

weight"), claim 2 ("with residence times ranging between 1 and 24 h", "with control of the chromaticity coordinates of the obtained pigment") and the features of claims 16, 17 and 20 as a whole is not referred to in the description. Claims 1, 2, 16, 17 and 20 are therefore not supported by the description as required by Article 6 PCT.

b. Claims 9 and 10 are unclear with regard to the word "optionally", as it is not clear whether the feature following the word "optionally" is a characterising feature of the embodiment claimed in the respective claim or not. Should the wording remain unamended, a novelty objection may be raised for said claims, because then the subject-matter of claims 9 and 10 is not distinguishable from the subject-matter of claim 1 (which is not novel).

c. Claim 13 is not clear, because the emphasising effect of "use of the micro silica" implies that the use of a certain micro silica material is envisaged; such a material is not defined, neither in the claim nor in the description.

d. It is not clear what the letter "X" is standing for on p. 2 l. 25 of the description.

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority must be indicated by the applicant on the line below:

IPEA/ European' Patent Office

WO12610-2

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA	Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION

Applicant's or agent's file reference: PCT-50

International application No.	International filing date *(day/month/year)*	(Earliest) Priority date *(day/month/year)*
PCT/ES99/00060	10 March 1999	

Title of invention: "PIGMENTS BASED ON SILICA AND IRON OXIDE AND PROCESS FOR THE MANUFACTURE THEREOF"

Box No. II APPLICANT(S)

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

ITACA, INNOVACIONES TECNICAS APLICADAS
A CERAMICAS AVANZADAS, S.A.
Partida Rambleta s/n
12191 - Puebla Tornesa
Castellón, Spain

Telephone No.:

Facsimile No.:

Teleprinter No.:

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

BAGAN VARGAS, Vicente
C/ Méndez Núñez, 23-2ºB
12002 - Castellón
Spain

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

BLASCO FUENTES, Antonio
Avda. Capuchinos, 6
12004 - Castellón
Spain

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

[X] Further applicants are indicated on a continuation sheet.

Internati nal application No.
PCT/ES99/00060

Continuation f Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

NEGRE MEDALL, Francisco
Avda. Hermanos Bou, 27-6ºC
12003 - Castellón
Spain

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

BELTRAN PORCAR, Vicente
C/ Ciscar, 31-8ºA
12003 - Castellón
Spain

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

CERVANTES RODRIGUEZ, Benito
Pza. Doctor Marañón, 1-8ºA
12005 - Castellón
Spain

State *(that is, country)* of nationality:	State *(that is, country)* of residence:
SPAIN	SPAIN

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:	State *(that is, country)* f residence:

☐ Further applicants are indicated on another continuation sheet.

See Notes to the demand form

International applicati n No.
PCT/ES99/00060

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is [X] agent [ ] common representative

and [X] has been appointed earlier and represents the applicant(s) also for international preliminary examination.

[ ] is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

[ ] is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

ELZABURU MARQUEZ, Alberto
Miguel Angel, 21
28010 - Madrid
Spain

Telephone No.: 91 700 94 00

Facsimile No.: 91 319 38 10

Teleprinter No.:

[ ] **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:*

1. The applicant wishes the international preliminary examination to start on the basis of:

[X] the international application as originally filed

the description [ ] as originally filed
[ ] as amended under Article 34

the claims [ ] as originally filed
[ ] as amended under Article 19 (together with any accompanying statement)
[ ] as amended under Article 34

the drawings [ ] as originally filed
[ ] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. [ ] The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opini n or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English

[ ] which is the language in which the international application was filed.

[ ] which is the language of a translation furnished for the purposes of international search.

[ ] which is the language of publication of the international application.

[X] which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

Th applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes n t to elect:

See Notes to the demand form

Sheet No. 4

International applicati n N . PCT/ES99/00060

Box No. VI CHECK LIST

The demand is accompanied by th following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

				For International Preliminary Examining Authority use only	
				received	not received
1. translation of international application	:	9	sheets	☐	☐
2. amendments under Article 34	:		sheets	☐	☐
3. copy (or, where required, translation) of amendments under Article 19	:		sheets	☐	☐
4. copy (or, where required, translation) of statement under Article 19	:		sheets	☐	☐
5. letter	:	1	sheets	☐	☐
6. other *(specify)*	:		sheets	☐	☐

The demand is also accompanied by the item(s) marked below:

1. [X] fee calculation sheet
2. [ ] separate signed power of attorney
3. [ ] copy of general power of attorney; reference number, if any:
4. [ ] statement explaining lack of signature
5. [ ] nucleotide and or amino acid sequence listing in computer readable form
6. [X] other *(specify)*: Additional representatives

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

Alberto de Elzaburu
Por Poder

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. ☐ The applicant has been informed accordingly.
4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. ☐ Although the date f receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/ES99/00060	For International Preliminary Examining Authority use only
Applicant's or agent's file reference PCT-50	Date stamp of the IPEA

Applicant: ITACA, INNOVACIONES TECNICAS APLICADAS A CERAMICAS AVANZADAS, S.A.

Calculation of prescribed fees

1. Preliminary examination fee	EUR 1,533	P
2. Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)*	EUR 148	H
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	EUR 1,681 TOTAL	

Mode of Payment

[X]	authorization to charge deposit account with the IPEA (see below)	[ ]	cash
[ ]	cheque	[ ]	revenue stamps
[ ]	postal money order	[ ]	coupons
[ ]	bank draft	[ ]	other *(specify)*:

Deposit Account Authorization *(this mode of payment may not be available at all IPEAs)*

The IPEA/ EPO [X] is hereby authorized to charge the total fees indicated above to my deposit account.

[X] *(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

28120008	6 October 2000	
Deposit Account Number	Date *(day/month/year)*	Signature

Form PCT/IPEA/401 (Annex) (July 1998)

See Notes to the fee calculation sheet

ADDITIONAL REPRESENTATIVE(S)

ADDITIONAL SHEET PERTAINING TO INTERNATIONAL PATENT APPLICATION N° PCT/ES99/00060 OF 10 MARCH 1999 IN THE NAME OF ITACA, INNOVACIONES TECNICAS APLICADAS A CERAMICAS AVANZADAS, S.A.

ADDITIONAL REPRESENTATIVES

Enrique Armijo

José Mª Alvarez

ALL WITH PROFESSIONAL PRACTICE AT MIGUEL ANGEL Nº 21, MADRID, SPAIN

PCT

PETITORIO

El abajo firmante pide que la presente solicitud internacional sea tramitada de conformidad con el Tratado de Cooperación en materia de Patentes.

Para uso de la Oficina receptora únicamente

U013610-2

Solicitud internacional Nº

Fecha de presentación internacional

Nombre de la Oficina receptora y "Solicitud internacional PCT"

Referencia al expediente del solicitante o del mandatario *(si se desea)* *(como máximo, 12 caracteres)*

Recuadro Nº I TITULO DE LA INVENCION "PIGMENTOS A BASE DE SILICE Y OXIDO DE HIERRO Y PROCEDIMIENTO DE FABRICACION DE LOS MISMOS"

Recuadro Nº II SOLICITANTE

Nombre y dirección: *(Apellido seguido del nombre; en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

ITACA, INNOVACIONES TECNICAS APLICADAS
A CERAMICAS AVANZADAS, S.A.
Partida Rambleta s/n
12191 - Puebla Tornesa
Castellón, España

☐ Esta persona es también un inventor.

Nº de teléfono

Nº de facsímil

Nº de teleimpresora

Estado de nacionalidad: ESPAÑA

Estado de domicilio: ESPAÑA

Esta persona es solicitante para: ☐ todos los Estados designados ☒ todos los Estados designados salvo los Estados Unidos de América ☐ los Estados Unidos de América únicamente ☐ los Estados indicados en el recuadro suplementario

Recuadro Nº III OTRO(S) SOLICITANTE(S) Y/O (OTRO(S)) INVENTOR(ES)

Nombre y dirección: *(Apellido seguido del nombre; en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

BAGÁN VARGAS, Vicente
C/ Méndez Núñez, 23-2ºB
12002-Castellón, España

Esta persona es:

☐ solicitante únicamente

☒ solicitante e inventor

☐ inventor únicamente *(Si se marca esta casilla, no se debe rellenar lo que sigue.)*

Estado de nacionalidad: ESPAÑA

Estado de domicilio: ESPAÑA

Esta persona es solicitante para: ☐ todos los Estados designados ☐ todos los Estados designados salvo los Estados Unidos de América ☒ los Estados Unidos de América únicamente ☐ los Estados indicados en el recuadro suplementario

☒ Los demás solicitantes y/o (demás) inventores se indican en una hoja de continuación.

Recuadro Nº IV MANDATARIO O REPRESENTANTE COMUN; O DIRECCION PARA LA CORRESPONDENCIA

La persona abajo identificada se designa/ha sido designada para actuar en nombre del/de los solicitante(s) ante las administraciones internacionales competentes como: ☒ mandatario ☐ representante común

Nombre y dirección: *(Apellido seguido del nombre; en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país.)*

ELZABURU, Alberto de
C/ Miguel Angel, 21
28010 Madrid, España

Nº de teléfono (34-91) 700-94-00

Nº de facsímil (34-91) 319-38-10

Nº de teleimpresora 22341 Elza E

☐ **Dirección para la correspondencia:** Márquese esta casilla cuando no se designe/se haya designado ningún mandatario o representante común y el espacio de arriba se utilice en su lugar para indicar una dirección especial a la que deba enviarse la correspondencia.

Continuación del recuadro Nº III OTROS SOLICITANTES Y/O (OTROS) INVENTORES

Si no se ha de utilizar ninguno de estos subrecuadros, esta hoja no debe ser incluida en el petitorio.

Nombre y dirección: *(Apellido seguido del nombre: en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

BLASCO FUENTES, Antonio
Avda. Capuchinos, 6
12004-Castellón, España

Esta persona es:
- [ ] solicitante únicamente
- [X] solicitante e inventor
- [ ] inventor únicamente *(Si se marca esta casilla, no se debe rellenar lo que sigue.)*

Estado de nacionalidad: ESPAÑA | Estado de domicilio: ESPAÑA

Esta persona es solicitante para: [ ] todos los Estados designados [ ] todos los Estados designados salvo los Estados Unidos de América [X] los Estados Unidos de América únicamente [ ] los Estados indicados en el recuadro suplementario

Nombre y dirección: *(Apellido seguido del nombre: en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

NEGRE MEDALL, Francisco
Avda. Hermanos Bou, 27-6ºC
12003-Castellón, España

Esta persona es:
- [ ] solicitante únicamente
- [X] solicitante e inventor
- [ ] inventor únicamente *(Si se marca esta casilla, no se debe rellenar lo que sigue.)*

Estado de nacionalidad: ESPAÑA | Estado de domicilio: ESPAÑA

Esta persona es solicitante para: [ ] todos los Estados designados [ ] todos los Estados designados salvo los Estados Unidos de América [X] los Estados Unidos de América únicamente [ ] los Estados indicados en el recuadro suplementario

Nombre y dirección: *(Apellido seguido del nombre: en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

BELTRÁN PORCAR, Vicente
C/ Ciscar, 31-8ºA
12003-Castellón, España

Esta persona es:
- [ ] solicitante únicamente
- [X] solicitante e inventor
- [ ] inventor únicamente *(Si se marca esta casilla, no se debe rellenar lo que sigue.)*

Estado de nacionalidad: ESPAÑA | Estado de domicilio: ESPAÑA

Esta persona es solicitante para: [ ] todos los Estados designados [ ] todos los Estados designados salvo los Estados Unidos de América [X] los Estados Unidos de América únicamente [ ] los Estados indicados en el recuadro suplementario

Nombre y dirección: *(Apellido seguido del nombre: en el caso de una persona jurídica, la designación oficial completa. En la dirección deben figurar el código postal y el nombre del país. El país de la dirección indicada en este recuadro es el Estado de domicilio del solicitante si no se indica más abajo el Estado de domicilio.)*

CERVANTES RODRÍGUEZ, Benito
Pza. Doctor Marañón, 1-8ºA
12005-Castellón, España

Esta persona es:
- [ ] solicitante únicamente
- [X] solicitante e inventor
- [ ] inventor únicamente *(Si se marca esta casilla, no se debe rellenar lo que sigue.)*

Estado de nacionalidad: ESPAÑA | Estado de domicilio: ESPAÑA

Esta persona es solicitante para: [ ] todos los Estados designados [ ] todos los Estados designados salvo los Estados Unidos de América [X] los Estados Unidos de América únicamente [ ] los Estados indicados en el recuadro suplementario

[X] Los demás solicitantes y/o (demás) inventores se indican en otra hoja de continuación.

Recuadro N° V DESIGNACION DE ESTADOS

A continuación se hacen las designaciones siguientes en virtud de la Regla 4.9.a) *(márquense las casillas adecuadas; debe marcarse por lo menos una)*:

Patente regional

☒ **AP** **Patente ARIPO:** **GH** Ghana, **GM** Gambia, **KE** Kenya, **LS** Lesotho, **MW** Malawi, **SD** Sudán, **SZ** Swazilandia, **UG** Uganda, **ZW** Zimbabwe, y cualquier otr Estado contratante del Protocolo de Harare y del PCT

☒ **EA** **Patente Euroasiática:** **AM** Armenia, **AZ** Azerbaiyán, **BY** Belarús, **KG** Kirguistán, **KZ** Kazakstán, **MD** República de Moldova, **RU** Federación de Rusia, **TJ** Tayikistán, **TM** Turkmenistán, y cualquier otro Estado contratante del Convenio sobre la Patente Euroasiática y del PCT

☒ **EP** **Patente Europea:** **AT** Austria, **BE** Bélgica, **CH y LI** Suiza y Liechtenstein, **CY** Chipre, **DE** Alemania, **DK** Dinamarca, **ES** España, **FI** Finlandia, **FR** Francia, **GB** Reino Unido, **GR** Grecia, **IE** Irlanda, **IT** Italia, **LU** Luxemburgo, **MC** Mónaco, **NL** Países Bajos, **PT** Portugal, **SE** Suecia, y cualquier otro Estado contratante del Convenio sobre la Patente Europea y del PCT

☒ **OA** **Patente OAPI:** **BF** Burkina Faso, **BJ** Benin, **CF** República Centroafricana, **CG** Congo, **CI** Côte d'Ivoire, **CM** Camerún, **GA** Gabón, **GN** Guinea, **ML** Malí, **MR** Mauritania, **NE** Níger, **SN** Senegal, **TD** Chad, **TG** Togo y cualquier otro Estado que sea Estado miembro de la OAPI y que sea un Estado contratante del PCT *(si se desea otra forma de protección o de tramitación, especifíquese en la línea de puntos)* .....

Patente nacional *(si se desea otra forma de protección o de tramitación, especifíquese en la línea de puntos)*:

☒ **AL** Albania .....
☒ **AM** Armenia .....
☒ **AT** Austria .....
☒ **AU** Australia .....
☒ **AZ** Azerbaiyán
☒ **BA** Bosnia y Herzegovina .....
☒ **BB** Barbados
☒ **BG** Bulgaria .....
☒ **BR** Brasil .....
☒ **BY** Belarús
☒ **CA** Canadá
☒ **CH y LI** Suiza y Liechtenstein
☒ **CN** China .....
☒ **CU** Cuba .....
☒ **CZ** República Checa .....
☒ **DE** Alemania .....
☒ **DK** Dinamarca .....
☒ **EE** Estonia .....
☒ **ES** España .....
☒ **FI** Finlandia .....
☒ **GB** Reino Unido
☒ **GE** Georgia .....
☒ **GH** Ghana .....
☒ **GM** Gambia
☒ **GW** Guinea-Bissau .....
☒ **HR** Croacia
☒ **HU** Hungría .....
☒ **ID** Indonesia
☒ **IL** Israel .....
☒ **IS** Islandia
☒ **JP** Japón .....
☒ **KE** Kenya .....
☒ **KG** Kirguistán .....
☒ **KP** República Popular Democrática de Corea .....
☒ **KR** República de Corea .....
☒ **KZ** Kazakstán .....
☒ **LC** Santa Lucía
☒ **LK** Sri Lanka
☒ **LR** Liberia
☒ **LS** Lesotho .....
☒ **LT** Tituania
☒ **LU** Luxemburgo
☒ **LV** Letonia
☒ **MD** República de Moldova .....
☒ **MG** Madagascar .....
☒ **MK** Ex República Yugoslava de Macedonia .....
☒ **MN** Mongolia
☒ **MW** Malawi .....
☒ **MX** México .....
☒ **NO** Noruega
☒ **NZ** Nueva Zelandia .....
☒ **PL** Polonia .....
☒ **PT** Portugal .....
☒ **RO** Rumania
☒ **RU** Federación de Rusia .....
☒ **SD** Sudán
☒ **SE** Suecia
☒ **SG** Singapur
☒ **SI** Eslovenia .....
☒ **SK** Eslovaquia .....
☒ **SL** Sierra Leona
☒ **TJ** Tayikistán .....
☒ **TM** Turkmenistán .....
☒ **TR** Turquía .....
☒ **TT** Trinidad y Tabago .....
☒ **UA** Ucrania .....
☒ **UG** Uganda .....
☒ **US** Estados Unidos de América .....
☒ **UZ** Uzbekistán .....
☒ **VN** Viet Nam .....
☒ **YU** Yugoslavia .....
☒ **ZW** Zimbabwe .....

Casillas reservadas para designar Estados (a los fines de una patente nacional) que han pasado a formar parte del PCT después de la publicación de la presente hoja:

☐ .....
☐ .....

Además de las designaciones arriba efectuadas, el solicitante efectuará también, en virtud de la Regla 4.9.b), todas las designaciones que estén permitidas con arreglo al PCT, salvo la designación o designaciones de _____ .

El solicitante declara que esas designaciones adicionales están sujetas a confirmación y que cualquier designación que no se confirme antes de que expiren los 15 meses a partir de la fecha prioritaria se considerará retirada por el solicitante al expirar dicho plazo. *(La confirmación de una designación consiste en la presentación de un aviso en el que se especifique dicha designación, así como el pago de las tasas de designación y confirmación. La confirmación deberá llegar a la Oficina receptora dentro de ese plazo de 15 meses.)*

Véanse las Notas al formulario del petitorio

Recuadro Nº VI REIVINDICACION PRIORIDAD ☐ Se indican otras reivindicaciones de prioridad en el recuadro suplementario.

Fecha de presentación de la solicitud anterior *(día/mes/año)*	Número de la solicitud anterior	Si la solicitud anterior es: solicitud nacional: país	solicitud regional:* Oficina regional	solicitud internacional: oficina receptora
Punto (1)				
Punto (2)				
Punto (3)				

☐ Se ruega a la Oficina receptora que prepare y transmita a la Oficina Internacional una copia certificada de la solicitud anterior/de las solicitudes anteriores *(sólo si la solicitud anterior ha sido presentada ante la oficina que actúa como oficina receptora de la presente solicitud internacional)* identificada(s) supra como punto o puntos: _____

* *Si la solicitud anterior es una solicitud ARIPO, se indicará en el recuadro suplementario por lo menos a un Estado miembro del Convenio de París para la Protección de la Propiedad Industrial para el que ha sido presentada la solicitud anterior (Regla 4.10.b)ii)). Véase el recuadro suplementario.*

Recuadro Nº VII ADMINISTRACION ENCARGADA DE LA BUSQUEDA INTERNACIONAL

Elección de la Administración encargada de la búsqueda internacional *(Si dos o más Administraciones encargadas de la búsqueda internacional son competentes para efectuar la búsqueda internacional, indíquese el nombre de la Administración elegida; se puede utilizar el código de dos letras)*: ISA / ES

Petición para que se utilicen los resultados de la búsqueda anterior; referencia a esa búsqueda *(si una búsqueda anterior ha sido realizada por o pedida a la Administración encargada de la búsqueda internacional)*:
Fecha *(día/mes/año)*: Número: País (u Oficina regional):

Recuadro Nº VIII LISTA DE VERIFICACION; IDIOMA DE PRESENTACION

La presente solicitud internacional contiene el siguiente número de hojas:

petitorio	:	4
descripción (excepto la parte de la lista de secuencias)	:	7
reivindicaciones	:	3
resumen	:	1
dibujos	:	1
parte de la lista de secuencias de la descripción	:	
Número total de hojas	:	16

La presente solicitud internacional está acompañada de los documentos que se identifican a continuación:

1. ☒ hoja de cálculo de tasas
2. ☒ poder separado firmado
3. ☐ copia del poder general; número de referencia, en su caso:
4. ☐ declaración que explica la ausencia de una firma
5. ☐ documento(s) de prioridad identificado(s) en el Recuadro Nº VI como punto o puntos:
6. ☐ traducción de la solicitud internacional en (idioma):
7. ☐ indicación separada relativa a microorganismos depositados u otro material biológico
8. ☐ lista de secuencias de nucleótidos y/o aminoácidos en formato legible por ordenador
9. ☒ otros *(especifíquese)*: Justificante pago de tasas.

Figura de los dibujos que debe acompañar el resumen: 1

Idioma de presentación de la solicitud internacional: Español

Recuadro Nº IX FIRMA DEL SOLICITANTE O DEL MANDATARIO

Junto a cada una de las firmas, indíquese el nombre de la persona que firma, así como su calidad (si dicha calidad no es evidente por lectura del petitorio).

Alberto de Elzaburu
Por Poder

Para la Oficina receptora únicamente

1. Fecha efectiva de recepción de la pretendida solicitud internacional:
2. Dibujos: ☐ recibidos: ☐ no recibidos:
3. Fecha efectiva de recepción, rectificada en razón de la recepción ulterior pero dentro del plazo, de documentos o de dibujos que completen la pretendida solicitud internacional:
4. Fecha de recepción, dentro del plazo, de las correcciones solicitadas según el Artículo 11.2) del PCT:
5. Administración de búsqueda internacional especificada por el solicitante: ISA /
6. ☐ Transmisión de la copia para la búsqueda diferida hasta que se pague la tasa de búsqueda.

Para uso de la Oficina Internacional únicamente

Fecha de recepción del ejemplar original por la Oficina Internacional:

Esta hoja no forma parte de la solicitud internacional y no cuenta una de sus hojas.

PCT

HOJA DE CALCULO DE TASAS

Anexo al petitorio

Para uso de la Oficina receptora únicamente

Solicitud internacional Nº

Sello con la fecha de la Oficina receptora

Referencia al expediente del solicitante o del mandatario: PCT-50

Solicitante: ITACA, INNOVACIONES TECNICAS APLICADAS A CERAMICAS AVANZADAS, S.A.

CALCULO DE LAS TASAS PRESCRITAS

1. TASA DE TRANSMISION . . . . . 10.040 [T]
2. TASA DE BUSQUEDA . . . . . 76.520 [S]

   Búsqueda internacional a efectuar por ISA/ES

   (Si dos o más Administraciones encargadas de la búsqueda internacional son competentes respecto de la solicitud internacional, indíquese el nombre de la Administración elegida para realizar la búsqueda internacional.)
3. TASA INTERNACIONAL

   Tasa de base

   La solicitud internacional contiene 16 hojas.

   30 primeras hojas . . . . . 68.000 [b_1]

   _____ (hojas siguientes) x _____ (cantidad adicional) = [b_2]

   Añadir las cantidades de las casillas b_1 y b_2 e inscribir el total en la casilla B . . . . . 68.000 [B]

   Tasas de designación

   La solicitud internacional contiene 75 designaciones.

   10 (número de tasas de designación pagaderas *(máximo 11)*) x 16.000 (importe de la tasa de designación) = 160.000 [D]

   Añadir los importes inscritos de las casillas B y D e inscribir el total en la casilla I . . . . . 228.000 [I]

   (Los solicitantes de ciertos Estados tienen derecho a una reducción del 75% de la tasa internacional. Si el solicitante tiene (o todos los solicitantes tienen) tal derecho, deberá(n) inscribir en la casilla I el 25% del total de las cantidades inscritas en las casillas B y D.)
4. TASA POR UN DOCUMENTO DE PRIORIDAD *(si fuere aplicable)* . . . [P]
5. TOTAL DE LAS TASAS PAGADERAS

   Añadir las cantidades inscritas en las casillas T, S, I, y P e inscribir el resultado en la casilla TOTAL . . . . . 314.560 TOTAL

☐ Las tasas de designación no se pagan en este momento.

FORMA DE PAGO

☐ autorización a cargar a la cuenta de depósito (véase infra)
☐ giro bancario
☐ cupones
☐ cheque
☒ efectivo
☐ otros *(especifíquese)*:
☐ giro postal
☐ timbres fiscales

AUTORIZACION RELATIVA A UNA CUENTA DE DEPOSITO *(este modo de pago puede no estar disponible en todas las Oficinas receptoras)*

La Oficina receptora/ ____

☐ está autorizada a cargar a mi cuenta de depósito el total de las tasas indicadas anteriormente.

☐ está autorizada a cargar a mi cuenta de depósito tod importe que falte o a abonar todo excedente en el pago del total de las tasas indicadas anteriormente.

☐ está autorizada a cargar a mi cuenta de depósito la tasa para la preparación y la transmisión del documento de prioridad a la Oficina Internacional de la OMPI.

Número de la cuenta de depósito _____ Fecha *(día/mes/año)* _____ Firma _____

Véanse las Notas relativas a la hoja de cálculo de tasas

AUTORIZACION

Los que suscriben VICENTE BAGAN VARGAS, ANTONIO BLASCO FUENTES, FRANCISO NEGRE MEDALL, VICENTE BELTRAN PORCAR, y BENITO CERVANTES RODRIGUEZ, con domicilio a efectos de notificaciones en Partida Rambleta s/n, 12191 Puebla Tornesa, Castellón, autorizan indistintamente a D. Alberto de Elzaburu, D. Fernando de Elzaburu, D. Alfonso Díez de Rivera Elzaburu o D. Antonio Tavira Montes-Jovellar, Agentes de la Propiedad Industrial, con domicilio profesional en calle Miguel Angel Nº 21, 28010 - Madrid, con facultad de delegar el encargo, para que, en su nombre y representación, firmen cuantas instancias, declaraciones y documentos presenten ante la Oficina Española de Patentes y Marcas, los modifiquen, reformen, renuncien o desistan ; recurran contra las resoluciones o acuerdos que recaigan y para que retiren los títulos y notificaciones a cuya expedición den lugar , todo ello en relación con la solicitud de Patente Internacional, por :

PIGMENTOS A BASE DE SILICE Y OXIDO DE HIERRO Y PROCEDIMIENTO DE FABRICACION DE LOS MISMOS.

Y cuanto más sea necesario hacer en cualquier tiempo, de conformidad con las instrucciones que al efecto puedan serles comunicadas.

Firmado en PUEBLA TORNESA, A 25 de FEBRERO de 199 9

Vicente Bagán Vargas

Benito Cervantes Rodríguez

Vicente Beltrán Porcar

Antonio Blasco Fuentes

ACEPTO ESTA AUTORIZACION

Alberto de Elzaburu
Por Poder

Francisco Negre Medall

AUTORIZACION

La que suscribe ITACA, INNOVACIONES TECNICAS APLICADAS A CERAMICAS AVANZADAS, S.A. con domicilio en Partida Rambleta s/n, 12191 Puebla Tornesa, Castellón, autoriza indistintamente a D. Alberto de Elzaburu, D. Fernando de Elzaburu, D. Alfonso Díez de Rivera Elzaburu o D. Antonio Tavira Montes-Jovellar, Agentes de la Propiedad Industrial, con domicilio profesional en calle Miguel Angel Nº 21, 28010 - Madrid, con facultad de delegar el encargo, para que, en su nombre y representación, firmen cuantas instancias, declaraciones y documentos presenten ante la Oficina Española de Patentes y Marcas, los modifiquen, reformen, renuncien o desistan ; recurran contra las resoluciones o acuerdos que recaigan y para que retiren los títulos y notificaciones a cuya expedición den lugar, todo ello en relación con la solicitud de Patente Internacional, por :

PIGMENTOS A BASE DE SILICE Y OXIDO DE HIERRO Y PROCEDIMIENTO DE FABRICACION DE LOS MISMOS.

Y cuanto más sea necesario hacer en cualquier tiempo, de conformidad con las instrucciones que al efecto puedan serles comunicadas.

Firmado en PUEBLA TORNESA, A 25
de FEBRERO de 199 9

Innovaciones Técnicas Aplicadas
a Cerámicas Avanzadas, S.A.

SR. VICENTE BELTRAN
CONSEJERO DELEGADO

ACEPTO ESTA AUTORIZACION

Alberto de Elzaburu
Por Poder

ELZABURU
Estnb 1865

Alberto de Elzaburu
† Fernando de Elzaburu
Alfonso D Rivera Elzaburu
Carlos Morán
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José I San Martín
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Manuel Illescas
Luis Baz
Ramón Cañizares
Víctor Carbayo
E Armijo Chávarri
Concepción Chacón
Ana Donate

I Arocas
A Vila
B de Haro
C Bonzom
AFD Rivera Elzaburu
J J Caselles
F Ilardia
I Andrade
R Torrecillas
L Moraleda
L Alonso
C Aguilera
J Ubeda-Romero
A Pérez
P Saturio
L Soriano
SD Rivera Elzaburu
J M Sainz de Marles
F J Saez
C Morán Medina

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y de Patentes Europeas
European Patent Attorneys
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Alemania

S/Your ref

N/Our ref
MIT/JL/ABV/PCT-50

Miguel Angel, 21
28010 Madrid 15 June 2001

FAX N° 00 49 89 2399 4465

Re : International Patent Application N° PCT/ES99/00060

Reply to written opinion according to Rule 66 PCT

1.- Amendments

New pages are enclosed herewith in response to the above opinion. The amendments made are detailed as follow:

Page 2, line 29: "X" letter has been removed (see Re Item VIII d. of the written opinion)
Page 3, line 21: the range of iron oxide exactly as disclosed in claim 1 of the application as formerly filed has been introduced (see Re Item VIII a. of the written opinion).
Page 3, line 32: uses of the pigments as disclosed in claims 16 and 17, and the chromatic coordinates of porcelain stoneware, as disclosed in claim 20, of the application as formerly filed, have been introduced (see Re Item VIII a.).
Page 5, line 10 the residence time as disclosed in claim 2 of the application as formerly filed, has been introduced (see Re Item VIII a.).
Page 5, line 22: Steps f) and g) of the patented process, as disclosed in claim 2 of the application as formerly filed, have been introduced (see Re Item VIII a.).
Page 8, claim 1: the term "... or fumed silica" has been removed (see Re Item V).
Page 8, claim 2: Raw materials have been restricted to those containing microsilica and iron oxide (see Re Item V). Support for that amendment exists in various paragraphs of the specification as formerly filed (pages 3-4, examples 1-4 and the abstract supplied).
Page 9, claims 9 and 10: the term "...optionally..." has been removed (see Re Item VIII b.)
Page 9, claim 13: the term "...the..." has been removed (see Re Item VIII c.).

Amendments made, in our opinion, do not contravene Article 19(2) and 34(2)(b) because the new paragraphs introduced into the description have all been taken from the text of the

claims as formerly filed, in order to meet Article 6 PCT, and the terms removed did not broaden the content of the specification as formerly filed but, by the contrary, restrict the scope sought.

Re Item V 2) Novelty (Article 33.1 and 2. PCT)

With the amendments introduced, the application now covers pigments, the manufacturing process thereof, the uses of those pigments and ceramic products and porcelain stoneware containing those pigments, in which the pigment composition is no longer based on fumed silica. D1 discloses pigments in which haematite is included in a fumed silica matrix. D2 discloses synthetic iron oxides obtained from copperas by calcinations, using fumed and precipitated silica. Fumed silica is a pyrogenic silica obtained from silanes calcination. Fumed silica has a high specific surface (300-400 m2/g in D1) and it is very expensive. The specific surface is a parameter which measures the reactivity of the silica. In the invention another type of silica (microsilica) is used, obtained as by-product of fumes in the manufacturing process of silicon and alloys thereof. Microsilica has surfaces much lower (0.015-20 m2/g) that fumed silica, being much cheaper as raw material. We enclose herewith extracts of articles published in the magazine Industrial Minerals, March and April 1989, wherein in table 5, page 52 and in page 41 (table on the top), a comparison of surface area between both type of silica is shown. Also along the text a comparison between the manufacturing processes used for both type of silica are disclosed with the technical features derived from them applicable to each silica. The aim of the invention, therefore, it is to get an alternative pigment made of iron oxide included in a silica matrix, wherein the source of silica is microsilica. Pigments obtained are cheaper than the ones existing in the market containing silica from a source of fumed silica. That lower price value is due to the fact that the silica source comes from the recovery of a by-product, microsilica, and its use in the pigment manufacturing. Moreover D1 is silent about the amount of silica present in pigment composition. The application is restricted to a silica content range of 70-98%. That high range, if compare, for example with D2 (0.25-10%), which also uses as source of silica, fumed silica, is due to the particular chemical characteristics of microsilica, in particular, to its low specific surface. Moreover, the low silica content of D2 would not allow to keep stable the iron oxide during the use of the pigment in the manufacturing of ceramic stoneware, for example, when temperatures higher than 1150°C are used. As matter of fact, D2 is restricted to calcinations temperatures ranging 718-871 °C. At temperatures over that range iron oxide is reduced with colour changing. Thus, D1 nor D2 disclose pigments with the composition of the invention, neither the source of silica was microsilica, but fumed silica, which, as explained, is a complete different chemical entity of completely different origin and with specific surface (reactivity) features distinguishable from microsilica. The invention therefore, it is a novel alternative to the existing prior art.

Re Item V 3) Inventive Step (Article 33.1 and 3. PCT)

The technical problem underlying the present invention is providing pigments of silica-iron oxide at cheaper price and with similar colour and stability features than the analogous pigments existing in the prior art. This problem is overcome by the present invention by the

use of microsilica as the silica source in a ratio of silica of 70-98 wt %. A person skilled in the art, by knowing the content of D1 or D2 or by combining the teachings of both documents would never arrive to the technical solution found in the invention, simply because both prior art documents use fumed silica as source of silica. Being that fumed silica of high reactivity (high specific surface) and expensive, the obvious solution to trap the iron oxide into the silica matrix to be formed at the cheapest possible price, would be to use the minimum of fumed silica in view of its high reactivity surface. The approach of the invention is precisely the opposite. In view of the fact that the microsilica is a by-product rather cheap, with a low reactivity surface, the silica content in the pigment is increased in order to assure the iron oxide stabilization during ceramic manufacturing involving very high temperatures processes. Thus the solution found in the invention would not appear as obvious to a man skilled in the art, by reading either D1 or D2 or both together in combination. Particularly important data to notice the non obviousness of the invention covered by the application can be found in D1 pg. 727 last paragraph and table 1. Colour, measured as L ranges in D1 30-50, a similar range obtained with the invention. In a similar range also of calcinations temperatures (1000-1200 °C). But, as it is said in D1, the stability pf pigments is **evidently** decreased when using silica having surface area lower than 300 m2/g. As it has been shown in the article provided, microsilica has a surface much lower than fumed silica but, surprisely, by using as disclosed in the invention, renders similar colour and stability features, at similar calcinations temperatures, for manufacturing pigments of iron oxide.

Obviously the process for obtaining a novel and inventive family of pigments, should be regarded as well as novel and inventive in all its variants. In a similar manner the use of those novel and inventive pigments and the ceramic products coloured with the aforesaid pigments, should also be regarded as novel and inventive.

We respectfully enclose herewith new replacement sheets wherein amendments have been made. We kindly request to have the opportunity of submit further amendments and/or arguments, according to Rule 66.4.(b) PCT.

ELZABURU

Dr. Manuel Illescas

Enclosures: New pages 1-10 of the Specification. (in triplicate with the confirmation of this fax).
Copies of Industrial Minerals, 1987, pages 39 and 41 (April) and page 52 (March).

PIGMENTS BASED ON SILICA AND IRON OXIDE AND PROCESS FOR THE MANUFACTURE THEREOF

Field of the Invention

The present invention relates to the technical field of pigment manufacturing. Specifically, it deals with obtaining silica and iron oxide pigments useful in different industries and particularly in the ceramics industry. The silica component of these pigments would be obtained from microsilica or from fumed silica as the most characteristic feature of the invention.

Description of the state of the art -

The natural pigments, silica B iron, have been known since ancient times for their chromophore properties. Extensively used in ceramics for colouring the mass, they provide a colour within the range of ochre B browns B oranges B reddish, on being introduced in high ratios which range from 2 to 12% by weight. However, they essentially lack homogeneity due to variations in the physico-chemical characteristics of the deposits.

Several efforts have been carried out trying to reproduce the features of this type of natural colorants, although these efforts have always come up against the limitation of achieving good quality products at a competitive cost relative to the market prices established for naturally occuring products.

In the prior developments there are different attempts to reproduce this type of colorants based on wet reaction processes, obtaining a gel, Fe_2O_3, $xSiO_2$, with a Fe_2O_3 content of 5 to 15% by weight, which must be submitted to a drying, calcination and milling process in order to obtain the product with an adequate quality.

In US patent 3,005,724 (1961), the starting product is a colloidal silica as a silica source, and a source of iron oxide, preferably iron sulphate, obtaining a suspension

which is gelified by the addition of an alkaline solution. This gel is dried and calcinated at temperatures between 900 and 14001 C and afterwards it is milled in order to obtain the pigment.

On the other hand, there are patents in which fumed silica is used to improve the features of the iron oxide synthetic pigments. In these cases, low silica ratios between 0.25 and 10 % of SiO_2 by weight are used, and it is used to improve the flowability and the coloration of the pigments in comparison with the synthetic iron oxides.

US patents 4,221,607 and 4,229,635, are disclosing processes for obtaining this type of iron oxide, starting from a solution of copperas as a source of iron oxide, to which a small proportion of silica is added (between 0.25 and 10% by weight) to obtain the iron oxide pigments with improved properties after a drying and calcination process. In US patent 4,221,607, the addition of silica is carried out before drying and calcination and an iron pigment is obtained which behaves better in the calcination process, while in US patent 4,229,635, the addition of iron is carried out after the calcination process and during a washing process of the colorant, before final drying and milling, obtaining a pigment with improved flowability.

References have not been found to the use of microsilica for the manufacture of silica-iron oxide pigments.

Brief description of the invention

The object of the present invention was to obtain inorganic pigments of the silica-iron oxide, Fe_2O_3 and SiO_2 system, using microsilica or fumed silica as the silica source, along with the process for industrial obtention of said pigment. The obtained pigments may have a of red B orange hue colouration, above all when used in the manufacture of ceramic products of low porosity such as porcelain stoneware. They are a competitive alternative, in

terms of quality and cost, to natural materials such as Thiviers stoneware, which are currently used. The presentation of the product is in the form of a micronised powder. The product can be incorporated into the base composition through a direct dispersion mechanism without the need for milling.

Detailed description of the invention

The colorants object of the invention consist mainly of mixtures of silicon oxide (silica), in ratios that range between 70 and 98 % by weight, and iron oxide, in different ratios, referred to a mixture of SiO_2 and Fe_2O_3.

This invention uses microsilica or fumed silica as the silicon oxide source. Which is basically obtained as a by-product by condensation of the gases evolved during the process of manufacturing silicon metal (electric arc melting) and alloys of silicon and other metals. Said product is characterised by its high content in silica (greater than 90 % expressed as SiO_2) and by its extremely fine particle size (around 100 nm).

As a source of iron oxide, red and/or yellow iron oxide (natural and/or synthetic) at ranges between 2 and 30% by weight can be used, or salts and/or complexes of iron that can be oxidised and/or decompose during the calcination process to provide iron oxide.

Small quantities of additive can be added to these basic mixtures to improve the features of the colorant and/or to modify its coloration.

The resulting colorants are pigments of a red-orange colour which can be used for colouring all sorts of materials, preferably ceramic materials, and specially ceramic masses that provide porcelain stoneware type low porosity ceramic materials. Particularly porcelain stoneware which show chromatic coordinates (Hunter-LAB) in the following ranges: L = 36-46, a = 10-18 and b = 7-11 are

obtained using those pigments of the invention. The pigments of the invention may be used, alone or in blends with other materials as integrant in the compositions or for the surface decoration of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

Depending on the composition, source of iron oxide, conditions of subsequent firing and treatment to which the colorant is submitted, a wide range of colours can be obtained within the red-orange tones.

In essence, the silica provides a protective coating layer for the iron oxide particles, protecting against external aggressions such as temperature, atmosphere and/or attack by other compounds. This protective layer ensures that the iron oxide processed in this way, remains more stable during its use in ceramic compositions that are submitted to high temperatures during their manufacture.

These colorants of silica-iron are obtained by calcination of mixtures of raw materials at high temperatures, forming a pigment with tridymite and/or crystobalite structure in which the iron oxide is incorporated with hematite structure. The tridymite or crystobalite are formed by calcination of the amorphous silica, obtaining a stable structure or another one, depending on the firing conditions and on the present additives and impurities.

The different compositions of raw material can be prepared through dry or wet processes. In the dry process, the mixture of raw materials is carried out in a mill or a blender. The resulting mixture may optionally be granulated to facilitate its handling (transport, dosing...). In the wet process, a suspension in water of the raw materials is prepared by milling and dispersion, drying the mixture in an atomisation process, in which an agglomerated material suitable for subsequent processing is obtained.

These mixtures of raw materials, more or less agglomerated, may optionally pass through a prior drying stage, to then proceed to calcination (thermal treatment at high temperature in which the different physico-chemical transformations that convert the material into its finished state will take place). Said calcination may be carried out in different oven types at temperatures comprised between 800 and 13001 C, depending on the features of the silica, the source of iron oxide and the used additives, with residence times ranging between 1 and 24h.

In some cases, a prior calcination may be effected, at a lower temperature to suitably prepare the raw materials for their subsequent reaction. In this stage, if necessary, the present organic material and the iron oxide are oxidised and/or the raw material acting as a source of iron oxide is decomposed.

After calcination the product is submitted to a particle size reduction step to provide a more homogeneous colour. Said operation is preferably carried out in a dry milling installation, with dynamic classification which permits to assure that more than 99 % of the particles are smaller than 40 micrometers. The process concludes with final blending with control of the chromaticity coordinates of the obtained pigment and dosing and packaging.

Examples

Example 1

87 kg of microsilica and 13 kg of synthetic red iron oxide are milled in a silex-ball mill for 4 hours with 50 litres of water. The suspension obtained is dried and the granulate obtained calcinated at a maximum temperature of 10501 C for three hours. A red coloured product is obtained, which is milled in a mill with alumina balls in dry conditions, until 99 % of the particles are smaller than 40 microns. This colorant, added to a standard composition of porcelain stoneware in a ratio of 5 % by weight, provides

fired pieces with Hunter-LAB chromaticity coordinates of L=38.0 a=15.6 b=7.4.

Example 2

346 kg of microsilica and 72 kg of synthetic red iron oxide are granulated in an intensive granulation machine with 80 litres of water. The granulate obtained is dried and calcinated at 10251 C for 6 hours at this maximum temperature. A reddish coloured product is obtained, which is milled in the same way as example 1. The chromaticity coordinates that are obtained are L=40.3, a=15.0 and b=7.3.

Example 3

94 kg of microsilica and 6 kg of synthetic red iron oxide are processed in the same way as in example 1. The chromaticity coordinates that are obtained are L=43.5, a=17.2 and b=8.5.

Example 4

A suspension is prepared with 65.8 kg of microsilica, 34.2 kg of ferrous sulphate ($FeSO_4\$7H_2O$) and 75.0 kg of water in a silex-ball mill. The milling lasts 4 hours. The suspension is dried and a granulate obtained that is pre-calcinated to decompose the sulphates and to oxidise the iron oxide and then the mixture is calcinated at 11001 C. The chromaticity coordinates that are obtained for the fired pieces prepared with 5% by weight of colorant are L.43.0, a=16.6 and b=10.5.

Description of the figures

Figure 1. Block diagram of the manufacturing process used.

1. Microsilica
2. Source of iron oxide
3. Milling
4. Agglomeration
5. Pre-calcination
6. Calcination

7. Cooling
8. Blending
9. Dry milling
10. Blending
11. Sacking

CLAIMS

1. Pigments of silica-iron oxide characterised in that the silica component (SiO_2) is obtained from microsilica, having a ratio of silica that ranges between 70 and 98% by weight, while the ratio of iron oxide ranges between 2 and 30% by weight.

2. A process for obtaining pigments of claim 1, characterised in that it comprises the following steps:

a) Blending the majority and minority raw materials, containing microsilica and iron oxide

b) Agglomerating of the resulting blend of raw materials from the previous stage

c) Calcinating in an oven the agglomerated blend obtained in the previous stage with a thermal cycle at temperatures comprised between 800 and 1300°C, with residence times ranging between 1 and 24 h,

d) Blending the pigment obtained in the previous calcination step,

e) Reducing the particle size of the obtained blend of pigment,

f) Final blending with control of the chromaticity coordinates of the obtained pigment,

g) Dosing and packaging.

3. A process according to claim 2, in which stages a) and/or b) may be carried out in dry conditions.

4. A process according to claim 2, in which stages a) and/or b) may be carried out in wet conditions.

5. A process according to claims 2 and 3, in which the blend from stage a) is carried out by milling.

6. A process according to claims 2 and 4, in which the mixture from stage a) is carried out by dispersion, preferably in water.

7. A process according to claims 2, 3 and 5, in which the agglomeration of stage b) consists of a granulation.

8. A process according to claims 2, 4 and 6, in which the agglomeration of stage b) consists of drying by atomisation.

9. A process according to claims 2 to 8, in which, before stage c) there is a prior pre-calcination step.

10. A process according to claims 2 to 9, in which, after stage c), there is a cooling step, prior to blending of the resulting pigment.

11. A process according to claims 2 to 10, in which step e) preferably consists of grinding or milling.

12. Pigments obtained according to the process of claims 2 to 11.

13. Use of microsilica as a source of SiO_2 in the manufacture of inorganic pigments and/or colorants.

14. Use of fumed silica as a source of SiO_2 in the manufacture of inorganic pigments and/or colorants.

15. Use according to claims 13 and 14, characterised in that the source of silica is obtained from condensation of gases evolved during the manufacture of silicon metal and/or alloys thereof.

16. Use of the pigments of claims 1 or 12, alone or in blends with other materials, as integrants in the compositions of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

17. Use of the pigments of claims 1 or 12, alone or in blends with other materials, in the surface decoration of enamels, glasses, ceramics, cements, plastics, laminates, graphic inks and rubber.

18. A ceramic product characterised in that it includes in its composition the pigments of claims 1 or 12.

19. A ceramic product in accordance with claim 18, characterised in that it consists of a porcelain stoneware.

20. A porcelain stoneware in accordance with claim 19, characterised in that it shows chromatic coordinates (Hunter-LAB) in the following ranges: L = 36-46, a = 10-18 and b = 7- 11, for a percentage pigment of 2% that gives a colour of red-orange tone.

ABSTRACT

Pigments based on silica and iron oxide and manufacturing process thereof. In order to obtain a pigment of silica-iron oxide, microsilica is blended and/or milled with a source of iron oxide in ratios between 2 and 30 % by weight of iron oxide. With the blending of raw materials a dry agglomerate is obtained that is calcinated at temperatures between 800 and 13001 C, obtaining a product that is milled to obtain a powder of red colour. This colorant can be used in a wide range of uses, for example, added to a standard porcelain stoneware composition, it allows red and orange coloured pieces to be obtained.

must be capable of purification to a maximum impurity level of around 300ppm, and for transparent silica it should be purified to a maximum of about 30ppm. The presence of TiO_2 in the chemical analysis may indicate the presence of rutile, needles of which could cause problems in drawing tubing by producing bubbles. In semi-conductor products the presence of heavy metals, which act as conductors, would be deleterious.

Particle size for the silica feed is very much dependent upon the fusion methods — torch, resistor furnace etc, and sand ranging from 50–500μ can be used. The ratio of silica raw material to fused silica product varies from 1:1 to 3:1.

Typical analysis of US high purity quartz sand

	ppm	
Al	20.0	
Fe	0.5	
Na	0.4	
K	0.4	
Ca	0.4	
Li	0.4	
Mg	1.0	
Ti	1.0	
Max. retained on 50 mesh screen		2%
Max. through 140 mesh screen		5%

Microsilica

Essentially microsilica is not produced directly from a silica mineral but is formed as a by-product of ferro-silicon or silicon production. However, the final quality of the microsilica by-product can be controlled to some extent by ensuring the purity of the silica raw material (quartz) used to manufacture the primary product. Microsilica is recovered from the hot waste gases produced during ferro-silicon or silicon manufacture in the following manner. SiO vapour mixes with oxygen in the upper, cooler part of the furnace, oxidises to form SiO_2 and condenses in the form of microspheres of amorphous silica. After passing through a pre-collector and cyclone to remove coarser particles, the material is blown into and collected in specially designed baghouse filters. The resultant product consists of finely divided amorphous silica spheres with a particle size similar to that of tobacco smoke. Average particle diameter is of the order of 0.15 microns.

Microsilica obtained as a by-product of silicon metal manufacture possesses a higher silica content (94–98% SiO_2) than that obtained from ferro-silicon production (about 85–90% SiO_2). Subsequently, consistency of product quality to ±2% can be further achieved by blending. Because of its by-product status microsilica has a considerable economic advantage over silica produced by other chemical means. The average price for untreated microsilica grades varies from around £150–250 per tonne.

Typical chemical composition of microsilica

% by weight	*Refractory grade*	*Concrete grade*
SiO_2	94–98	85–96
Fe_2O_3	0.1–0.4	0.2–3.0
Al_2O_3	0.02–0.4	0.2–0.5
CaO	0.1–0.4	0.1–0.7
MgO	0.2–0.9	0.3–3.5
Na_2O	0.1–0.4	0.2–1.8
K_2O	0.2–0.7	0.4–3.5
C	0.2–1.3	0.4–2.3
MnO	—	—
LOI	0.05–2.5	0.7–4.0

Source: Concrete, October 1986

About 120,000 tpa of high quality microsilica is available for use, derived from silicon and ferro-silicon manufacture. The material is characterised by a very small particl size (average diameter 0.15μ), spherical particles, and a very high surface area (about 20 sq metres per g). These attributes combine to make microsilica a highly reactive silica product. Because of their siz and shape particles are able to move between and around coarser particles, filling even the most minute spaces in any mixture. There are consequently several areas of application for which microsilica is particularly well suited.

Cementitious applications

In cementitious compositions the microsilica particles act as a superpozzolan as well as filler, converting less useful calcium hydroxide crystals into calcium silicate hydroxide gel binder. This results in an improved microstructure because of the denser pore structure, which in turn results in reduced permeability, increased durability, and higher strength. Bonding to aggregate and reinforcing materials increases and in fibre-reinforced products the fibre durability is also improved.

Glossary

Amorphous silica is often used with reference to the naturally occurring mineral tripoli which is mined exclusively in Illinois and Missouri in the USA. This is indeed a misnomer since tripoli is a microcrystalline silica in which no amporphous particles have been detected. True amorphous silicas include precipitated silica, fumed silica, silica gel, and glassy minerals such as expanded perlite. It also includes materials such as microsilica spheres which are obtained as a by-product from silicon and ferro-silicon manufacture.

- **Fumed silica** is an amorphous synthetic silica ie. it is not produced directly from a naturally occurring silica mineral, but is a chemically derived product. Fumed silica can be produced from the reaction of ferro-silicon with hydrochloric acid to produce silicon tetrachloride which is subsequently hydrolised in a flame of hydrogen and oxygen to produce silica. This product is also known as pyrogenic or colloidal silica. The cost of fumed silica (at about £4 per kg) is greater than that of microsilica which is essentially a by-product and commands prices in the region of less than £1 per kg. Fumed silica will be considered in the context of this article only in those areas of application which overlap with naturally occurring silicas.

- **Microsilica** will be used in the context of this feature to refer to the silica spheres obtained as a by-product of silicon and ferro-silicon manufacture. As such they will also be discussed alongside natural silica minerals since they are essentially obtained as a primary product from silica sand rather than being chemically derived. The term will not be applied to any naturally occurring silica mineral. In other literature microsilica products are also referred to as volatised, arc furnace, pyrogenic, and fume silica.

Precipitated silica is a synthetically produced amorphous silica obtained from the reaction of water glass (sodium silicate) with carbonic or sulphuric acid. The sodium silicate is prepared by heating silica sand which has been pre-reacted with caustic soda. The product is then diluted to produce water glass. Silica sand raw material requirements for this application specify a minimum 99% silica content, maximum 0.45% alumina, and maximum 0.1% Fe_2O_3. The size requirement is for 100% less than 20 mesh.

Pyrogenic silicas

A synthetic version of silica can be produced by an electric arc process with a charge of quartz and coke but apart from minor usage by *F. B. Goodrich Co.* in the USA and Degussa in West Germany, this process has not been a truly commercially viable one. The most important pyrogenic silicas are derived from silicon tetrachloride (also known as tetrachlorosilane), itself produced from silicon metal (or in some cases ferrosilicon) for which the starting raw material is lump quartz.

Fumed silica

Fumed silica is prepared by the high-temperature hydrolysis of silicon tetrachloride in a flame of hydrogen and oxygen. The resultant silica consists of very fine spherical particles of an even size (typically in the 7–20 nanometre range). Primary particles are often joined together in aggregates or chains and most importantly the outer surfaces are populated by hydroxyl ions.

When fumed silica is dispersed in liquid systems, its surface hydroxyl ions can link the individual aggregates into intricate, three-dimensional networks which result in thickening or gel formation. Since the linkages may be easily broken (by shear) and re-established the product is an excellent example of a thixotropic material.

When blended into powder systems, fumed silica works as an anticaking and free-flowing agent — since its fine particle size and high surface area enable it to cover the large particles of powder with a thin coating.

Other silicon-metal-derived products

Silicon metal provides the starting point for a number of high purity silicon compounds including silanes, silicones, fumed silica (described above), and semiconductor silicon. The intermediate product for most of these compounds is silicon tetrachloride (or tetrachlorosilane).

Silicones

The silicones, or polysiloxanes, are chemical polymers in which atoms of silicon and oxygen form the central chain (rather than carbon as in "conventional" organic polymers). In most silicones two organic groups — usually methyl ($-CH_3$) or phenyl ($-C_6H_5$) — are attached to each silicon atom. They range from oily liquids to rubbery solids and are stable toward heat, water repellant, chemically inert, and electrically insulating. Silicones are used as lubricants, hydraulic fluids, electrical insulators, and moisture-proofing agents.

The main manufacturing process involves the reaction between methyl chloride with powdered silicon metal powder (in the presence of copper/copper oxide catalysts) to produce a mixture of chlorosilanes, which are separated by fractional distillation. The different chlorosilanes, which have the general formula R_nSiCl_{4-n}, can then be polymerised by controlled hydrolysis.

Silanes

The silanes are a series of covalently bonded compounds containing silicon and hydrogen with the general formula Si_nH_{2n+2} and the simplest member is monosilane, SiH_4. The silanes are structural analogues of the saturated hydrocarbons but are much less stable. Pure silanes can be made by the reaction between magnesium silicide and acid or between silicon tetrachloride and lithium aluminium hydride; they are highly unstable and burn or explode on contact with air. The chlorosilanes are important intermediate compounds and may also be used in direct application to impart water repellancy to other materials.

Semiconductor silicon

The purification process to convert silicon metal into super-pure semiconductor silicon begins with the production of an intermediate compound such as trichlorosilane ($SiHCl_3$) or tetrachlorosilane ($SiCl_4$) which is then purified by fractional distillation. The purified distillate is then pyrolytically decomposed in an atmosphere of hydrogen to yield super-pure silicon metal and hydrochloric acid:

$$H_2 + SiHCl_3 \rightarrow Si + 3HCl$$

The polycrystalline silicon thus formed is converted to single crystal by the Czochralski or floating-zone method.

Table 5. Typical properties of synthetic silicas

	Silica gel	*Pptd silica*	*Pptd silicates NaAl*	*Pptd silicates Ca*	*Fumed silica*
SiO_2, %	99.5	98.0–99.5	82	78	99.8 min
Na_2O %		0.2–1.0	9	2	
Al_2O_3			9		<0.05
CaO				18	
Fe_2O_3, %	0.01	<0.03	<0.03	<0.03	<0.003
SO_3 %		0.7–0.8	0.5	0.5	
LOI	3–15	3–7	6–12		1–3
Surface area BET, m^2/g	250–850	25–300	35–100		50–400
Average particle size (nanometers)	5–20	6–60	5–30		5–50
Pore diameter (angstroms)	20–200	>800			
Specific gravity	2.0	2.0	2.1		2.2
pH	3–8	5–9	10–11		3.6–4.3
Whiteness %		97	97		

Sources: Crosfield Chemicals, Degussa, Rhône-Poulenc, Cabot Corp.

Comparison of cementitious materials available in the UK

	Microsilica	OPC	PFA	GGBFS
Chemical (% by weight)				
SiO_2	92.0	20.0	50.0	38.0
Fe_2O_3	1.2	3.5	10.4	0.3
Al_2O_3	0.7	5.0	28.0	11.0
CaO	0.2	65.0	3.0	40.0
MgO	0.2	0.1	2.0	7.5
Na_2O+K_2O	2.0	0.8	3.2	1.2
Physical				
Surface area (m^2/kg)	15–20,000	350–500	300–600	300–500
Bulk density (kg/m^3)	200–300	1300–1400	1,000	1,000–2,000
Specific gravity	2.20	3.12	2.30	2.90

OPC ordinary portland cement; PFA pulverised fuel ash.
GGBFS ground granulated blast furnace slag.
Source: Elkem literature.

There is currently no British Standard for microsilica or microsilica concretes. However ASTM C618, which presents the requirements for fly ash and raw or calcined natural pozzolan used as mineral admixtures in portland cement concrete, is being updated to include microsilica. In Norway and Canada, where the bulk of microsilica is produced, standards do exist (NS 3050:1976, NS3474:1978, and A23.SM:1981). Some recommendations for microsilica have been derived from the British Board of Agrément Certificate.

SiO_2 content	85% minimum
Alkali content as Na_2O	2% maximum
Carbon content	2% maximum
% passing 45μ sieve	99% minimum
Solid content of slurries	50%±2%
pH of slurries	5.5±1

Overall, microsilica can offer a number of beneficial effects to concrete mixes including — total suppression of alkali silica reaction, reduction of permeability, sulphate resistance, reduced chloride ion penetration from 50% to 100%, corrosion inhibition, reduced carbonation, greatly improved freeze-thaw durability, improved workability and pumpability, increased chemical and abrasion resistance, and increased compressive, flexural, and tensile strengths.

Polymer applications

Microsilica particles function as effective reinforcing fillers in extruded polymer products, serving to improve their impact resistance and stiffness. Special microsilica products with matched chemical additives are also produced which contribute to a smoother production process and increased productivity.

Refractory applications

Only the highest microsilica grades produced from silicon metal manufacture are used in refractory applications because of its higher price and limited availability. These grades are used in refractory concretes made from calcium aluminate cements and in other refractory materials eg. castables and bricks, where they improve the hydraulic and ceramic bonding of these products thereby enhancing other properties Increasingly, refractory castables containing microsilica are replacing refractory bricks in many areas. Whilst conventional castables hav limitations relating to their physical, mechanical, and thermal properties because of their water and calcium contents, the addition of microsilica reduces the am unt of calcium aluminate required and consequently the water content. As a result microsilica castables can achieve strengths some three or four times higher than conventional materials. The new range of castables, which have microsilica contents varying from 2% to 12% by weight and calcium aluminate contents of 0–10% by weight, possess high mechanical strength, high resistance to mechanical abrasion, excellent resistance to thermal shock because of the even expansion characteristics, low shrinkage due to low water content, and a low apparent porosity.

Microsilica is additionally being used in monolithic linings and precast shapes and allows their production by new techniques thereby eliminating the need for firing before installation. In high alumina bricks the addition of microsilica reduces the need for water, its high reactivity improves the ceramic bonding so that firing temperatures can be lowered by about 100–150°C, and the dense packing improves product resistance to chemical and abrasive wear. Microsilica improves adhesion in castables and minimises rebound loss when used as a gunning refractory material.

Overall, the high strength of microsilica-based castable refractories makes it possible to considerably reduce the lining thickness in most kilns, furnaces, boilers, and preheaters. Despite being a relatively now additive material in the refractories industry a large number of applications have been found in the steel and foundry, cement, petroleum and petrochemical, ceramic, glass, and pulp industries. Additionally, special application areas have been identified eg. in incinerators and power station boilers.

Other uses

The high reactivity of microsilica is found to give economic benefits in the production of various silicates whilst it is also used as coating powders, insulating powders, aids to catalyst support systems, and for selective adsorption of ions in the chemical industry.

Filler and extender applications

Silica in its finest forms, as a flour, microsilica, precipitated, and fumed finds application in reinforcement filler and extender applications. Here the particle size and surface area of th silica are two of its most important attributes. Tripoli is produced in a variety of grades ranging from 99% less than 74μ to 99% less than 10μ and there is also the likelihood of even smaller grades being produced. Its purity is high, averaging about 98–99% SiO_2, 0.1–1% Fe_2O_3 according to the source (Missouri-Oklahoma "rose" or "cream" tripoli has the higher iron content whilst the Illinois white variety has the lower), and less than 1% alumina. The ultimate particle size is sub-micron but tripoli particles tend to agglomerate to form porous aggregates. Precipitated silica similarly is composed of aggregates of sub-micron particles (average diameter 0.019μ) which agglomerate to form larger clusters. Silica content of the grades varies from 87% to 97.5%. Precipitated silicas currently sell for around $0.4–0.5 per lb. Fumed silica, also found in agglomerated form, has particles with nominal diameters ranging from 0.014–0.007μ and a silica content averaging more than 99.8%. The cost of fumed silica is around £4 per kg.

Plastic

Silica flour and tripoli are used to impart flexural and compressive strength to plastics. In addition, their low oil absorption, wettability, and rapid dispersion allow high loading in most compounds. Silica additions improve dimensional stability and improve resistance to thermal shock. One problem identified with the use of these products, however, is wear on extruding nozzles and moulds. It is anticipated that finer gradings should overcome this drawback. The excellent dielectric properties of tripoli also make it suitable for plastics used to encapsulate electronic components.